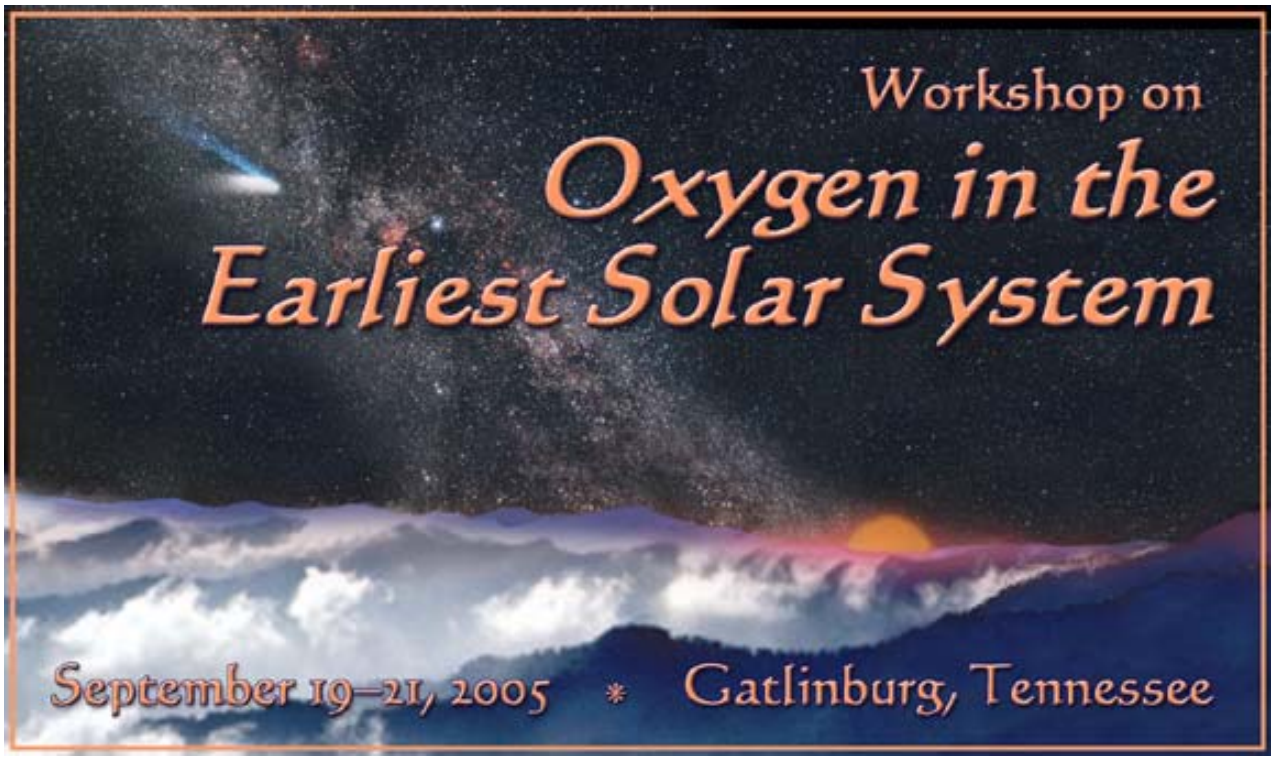


Workshop Program and Abstracts

LPI Contribution No. 1278

Workshop on
Oxygen in the Earliest Solar System

September 19–21, 2005
Gatlinburg, Tennessee

✸ ✧ ✸ ✧ ✸ ✧ ✸

This workshop is dedicated to Dr. Robert N. Clayton, who was not only a pioneer in the study of solar system oxygen but continues to be a leader in this field

✸ ✧ ✸ ✧ ✸ ✧ ✸

Sponsored by

Lunar and Planetary Institute
National Aeronautics and Space Administration

Convener

Glenn MacPherson, *Smithsonian Institution*

Earliest Solar System Materials Team, Outer Planets Team, and Workshop Program Committee

Robert Clayton, *University of Chicago*
Andrew Davis, *University of Chicago*
Pascale Ehrenfreund, *Leiden Observatory*
Bruce Fegley, *Washington University*
Walter Huebner, *Southwest Research Institute*
Jonathan Lunine, *University of Arizona*
Glenn MacPherson, *Smithsonian Institution*
Stephen Mackwell, *Lunar and Planetary Institute*
Scott R. Messenger, *NASA Johnson Space Center*
Julianne Moses, *Lunar and Planetary Institute*
Larry Nittler, *Carnegie Institution*
James Papike, *University of New Mexico*
Sara Russell, *Natural History Museum, London*
Ed Scott, *University of Hawai'i at Manoa*

Lunar and Planetary Institute 3600 Bay Area Boulevard Houston TX 77058-1113

LPI Contribution No. 1278

Compiled in 2005 by
LUNAR AND PLANETARY INSTITUTE

The Institute is operated by the Universities Space Research Association under Agreement No. NCC5-679 issued through the Solar System Exploration Division of the National Aeronautics and Space Administration.

Abstracts in this volume may be cited as

Author A. B. (2005) Title of abstract. In *Workshop on Oxygen in the Earliest Solar System*, p. XX. LPI Contribution No. 1278, Lunar and Planetary Institute, Houston.

This volume is distributed by

ORDER DEPARTMENT
Lunar and Planetary Institute
3600 Bay Area Boulevard
Houston TX 77058-1113, USA
Phone: 281-486-2172
Fax: 281-486-2186
E-mail: order@lpi.usra.edu

Mail orders requestors will be invoiced for the cost of shipping and handling.

ISSN No. 0161-5297

Preface

This volume contains abstracts that have been accepted for presentation at the Workshop on Oxygen in the Earliest Solar System, September 19–21, 2005, Gatlinburg, Tennessee.

Administration and publications support for this meeting were provided by the staff of the Publications and Program Services Department at the Lunar and Planetary Institute.

Contents

Monday, September 19, 2005
WELCOME AND INTRODUCTION
8:00 a.m.

8:00 a.m. MacPherson G. J.
Welcome and Introductory Remarks

8:10 a.m. Clayton R. N. *[INVITED]
Historical Perspective — The Unique Role of Oxygen in the Earliest Solar System **[#9006]**

EXTRASOLAR OXYGEN

Chair: D. D. Clayton

8:40 a.m. Introduction

8:55 a.m. Meyer B. S. *[INVITED]
Nucleosynthesis and Galactic Chemical Evolution of the Isotopes of Oxygen **[#9022]**

9:25 a.m. Snow T. P. * Jensen A. G. [INVITED]
Oxygen in the Diffuse Interstellar Medium **[#9020]**

9:55 a.m. Break

10:10 a.m. Markwick-Kemper F. *[INVITED]
The Formation and Processing of Interstellar Oxygen-rich Dust **[#9002]**

10:40 a.m. Nittler L. R. *[INVITED]
Presolar O-rich Dust Grains in the Solar System **[#9023]**

11:10 a.m. General Discussion

Monday, September 19, 2005
OXYGEN IN THE SUN
11:25 a.m.

Chair: A. M. Davis

11:25 a.m. **Introduction**

11:40 a.m. Hashizume K. * Chaussidon M. [INVITED]
Oxygen Isotope Composition of Solar Wind Implanted in Lunar Soils: A ^{16}O-rich Protosolar Nebula **[#9003]**

12:10 – 1:15 p.m. **LUNCH**

1:15 p.m. Ireland T. R. *[INVITED]
Oxygen-16 Variations in the Solar System: The Positives and Negatives **[#9015]**

1:45 p.m. Burnett, D. S. * Genesis Science Team [INVITED]
Status of Oxygen Isotope Measurements from Genesis Solar Wind Samples **[9032]**

2:15 p.m. Allende Prieto C. * Lambert D. L. [INVITED]
The Revised Solar Abundance of Oxygen **[#9030]**

2:45 p.m. **Discussion**

3:00 p.m. **Break**

Monday, September 19, 2005
SOLAR NEBULA REDOX CONDITIONS
3:15 p.m.

Chair: E. Scott

3:15 p.m. **Introduction**

3:30 p.m. Grossman L. * [INVITED]
Redox Conditions During Nebular Condensation **[#9009]**

4:00 p.m. Simon S. B. * Sutton S. R. Grossman L.
Valence of Ti and V in Fassaite: A Recorder of Oxygen Fugacity During Crystallization of Coarse-grained Refractory Inclusions **[#9017]**

4:15 p.m. Ciesla F. J. * Krot A. N. Petaev M. I. [INVITED]
Astrophysical Modeling of the Distribution of Water in Protoplanetary Disks: Implications for Nebular Redox Conditions and Oxygen Isotopes **[#9012]**

4:45 p.m. Wong M. H. * Atreya S. K. Mahaffy P. R. [INVITED]
Oxygen and Other Volatiles in Jupiter: Insights into the Early Solar System **[#9031]**

5:15 p.m. Johnson T. V. * Lunine J. I. [INVITED]
Densities of the Saturnian Satellites and the C/O Chemistry of the Solar Nebula **[#9027]**

5:45 p.m. **Discussion**

Tuesday, September 20, 2005
COMETS AND INTERPLANETARY DUST PARTICLES
8:30 a.m.

Chair: S. R. Messenger

8:30 a.m. **Introduction**

8:45 a.m. Sandford S. * [INVITED]
Interstellar Heritage of Cometary Composition **[#9033]**

9:15 a.m. Messenger S. * Keller L. P. [INVITED]
Oxygen Isotopic Insights into Origins and Histories of Cometary Materials **[#9024]**

9:45 a.m. DiSanti M. A. * Dello Russo N. [INVITED]
Astronomical and Spectroscopic Perspective of Comets: Direct Detection of Oxygen-bearing Parent Volatiles at Infrared Wavelengths **[#9011]**

10:15 a.m. **Break**

10:30 a.m. Keller L. P. * [INVITED]
Transition Element (Fe, Cr, and Mn) Oxidation States Recorded in Primitive Interplanetary Dust **[#9025]**

11:00 a.m. Altwegg K. * Balsiger H. [INVITED]
Oxygen Isotopes in the Volatile Material of Comets **[#9008]**

11:30 a.m. **Discussion**

12:00. – 1:00 p.m. **LUNCH**

Tuesday, September 20, 2005
OXYGEN ISOTOPES IN CHONDRITIC COMPONENTS
1:00 p.m.

Chair: G. J. MacPherson

1:00 p.m. **Introduction**

1:15 p.m. Yurimoto H. * Itoh S. Krot A. N. [INVITED]
Oxygen Isotopic Characteristics of Refractory Inclusions **[#9019]**

1:45 p.m. Guan Y. * Hsu W. Ushikubo T. Leshin L. A.
Oxygen Isotopes of Individual Minerals in the Pink Angel **[#9028]**

2:00 p.m. Aléon J. * El Goresy A. Zinner E.
First Evidence for Co-Existing ^{16}O-poor and ^{16}O-rich Gases in the Early Solar Nebula Inferred from a Compound Ca-Al-rich Inclusion from Efremovka **[#9004]**

2:15 p.m. Krot A. N. * Jones R. H. Yoshitake M. Yurimoto H. [INVITED]
Oxygen Isotopic Compositions of Chondrules **[#9014]**

2:45 p.m. **Break**

3:00 p.m. Aléon J. * Duprat J. Robert F. Toppani A. Derenne S.
Extreme Oxygen Isotope Ratios in Silica-rich Grains from Carbonaceous Chondrites: A Multi-Approach Study **[#9005]**

3:15 p.m. Kunihiro T. * Nagashima K. Brearley A. Yurimoto H. [INVITED]
Oxygen Isotopes of Matrix of Primitive Meteorites and Implications to Nebular Dust **[#9026]**

3:45 p.m. Choi B.-G. * Cosarinsky M. Wasson J. T. [INVITED]
Oxygen Isotopes of Secondary Phases in Unequilibrated Chondrites: Implication for the Fluids/Ices in the Nebula and Asteroids **[#9013]**

4:15 p.m. **Discussion**

Wednesday, September 21, 2005
UNDERSTANDING OXYGEN ISOTOPIC FRACTIONATIONS
IN THE SOLAR NEBULA
8:30 a.m.

Chairs: J. R. Lyons

8:30 a.m. **Introduction**

8:45 a.m. Kuramoto K. * Yurimoto H. [INVITED]
Oxygen Isotopic Evolution During the Formation and Evolution of the Solar Nebula: Molecular Cloud Origin Hypothesis for the Isotopic Anomaly and Its Implications **[#9016]**

9:15 a.m. Bergin E. A. *
High Energy Radiation Fields Impinging the Surfaces of Protoplanetary Disks **[#9001]**

9:30 a.m. Lyons J. R. * [INVITED]
CO Self-shielding in the Solar Nebula **[#9021]**

10:00 a.m. **Break**

10:15 a.m. Young E. D. * [INVITED]
H_2O Transport and $\Delta^{17}O$ in the Solar Nebula **[#9010]**

10:45 a.m. Fukui T. Kuramoto K.
Evolution of Oxygen Isotopic Composition and C/O Ratio at Late Stage of Proto-Planetary Accretion Disk **[#9018]**

11:00 a.m. Marcus R. A. * [INVITED]
Mass-Independent Gas Phase and Surface Reactions of Geochemical and Cosmochemical Interest **[#9007]**

11:30 a.m. Davis A. M. * McKeegan K. D. [INVITED]
Experimental Constraints on High Temperature Oxygen Isotopic Exchange and on Mass Dependent Isotopic Fractionation and Redox Conditions During Evaporation **[#9029]**

12:00 noon **Discussion**

EXTREME OXYGEN ISOTOPE RATIOS IN SILICA-RICH GRAINS FROM CARBONACEOUS CHONDRITES : A MULTI-APPROACH STUDY. J. Aléon[1], J. Duprat[2], F. Robert[3], A. Toppani[4] and S. Derenne[5], [1]CRPG-CNRS, 15 rue Notre-Dame des Pauvres, 54501 Vandoeuvre-les-Nancy, France (aleon@crpg.cnrs-nancy.fr), [2]CSNSM, Bat 104, 91405 Orsay Campus, France, [3]LEME-MNHN, 61 rue Buffon, 75005 Paris, France, [4]IGPP-LLNL, 7000 East avenue L413, Livermore CA 94550, USA, [5]LCBOP-ENSCP, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France.

Introduction: Extreme isotopic variations (up to several orders of magnitude) in minute meteoritic grains are usually attributed to stellar nucleosynthesis before the birth of the solar systeme [e.g. 1]. Micrometer-sized silica-rich grains with ^{17}O and ^{18}O excesses up to a factor 200 were recently discovered emebedded in the refractory organics of the Murchison meteorite [2]. These grains were found to account for almost 1 ppm of the host meteorite, as much as all other presolar oxide grains (with the exception of silicates) [3-5]. Contrary to typical presolar grains, oxygen in these silica-rich grains was found to be a mixing between only two reservoirs : an extreme anomalous oxygen reservoir and a solar or close to solar reservoir. Similar extreme compositions were observed in an unusual post-asymptotic-giant-branch star [6] but conventional AGB star nucleosynthesis models fail to explain these observations. Because all grains must have come from a single source, assuming they are presolar require that the young Sun encountered an unusual post-AGB star. By contrast nucleosynthesis upon irradiation of the circumsolar gas by particles with characteristics of impulsive flares produce the expected composition. In order to establish whether these grains are presolar and come from a single unusual star or if they were formed in the vicinity of the young Sun by the selective trapping of an irradiated gas, we investigated several tracers: (1) D/H with C/H ratios and $^{15}N/^{14}N$ with C/N ratios were mapped by IMS 1270 ion probe to search for large isotopic anomalies, (2) an ion probe depth profile for O isotopes was done to investigate possible heterogeneities at the 10-20 nm scale, (3) a sample of insoluble organic matter from Orgueil was studied and finally (4) we started a mineralogical study of the grains by transmission electron mircoscopy.

Results: *O isotopcs mapping in the insoluble organic matter from Orgueil*. No anomalous silica-rich grains were found in Orgueil. With the extraction yield and the mapped area, the abundance of these grains was found to be less than ~50 ppb, at least a factor of 10 less than in Murchison.

O isotopes depth profiling. Depth profiling over complete erosion of two grains reveal the absence of sharp isotopic contrast indicative of subgrains or isotopic heteorgeneities. By contrast both grains show a smooth profile with lower isotopic ratios at the beginning of the analysis and at the end. The final decrease can easily be attributed to the erosion of the grains and the rapid increase at the beginning suggests that a significant amount of contamination was removed.

Nitrogen isotopic mapping. No significant isotopic anomaly was found (within a factor 2). The low ion yields and the similarity with the surrounding organics suggests that these elements are dominated by contamination from the meteoritic IOM. If present isotopic anomalies must be small and at low concentrations.

Hydrogen isotopes. Again H isotopes were found to be similar to the surrounding organic material but C/H ratios in the grains were lower by a factor 10 indicative of an hydrated component in the grains. Whether this component is truly indigenous or results from terrestrial hydration still remains to be determined.

TEM mineralogy. Two residual grains were sectioned using a Focused Ion Beam and examined by TEM. Preliminary results indicates that these grains are amorphous silica. A more extensive study is required to better understand their formation.

Conclusions: More detailed results will be presented at the meeting, but these preliminary observations suggests that, as already observed for Si and Mg [2,7], the silica-rich grains lack exotic isotopic compositions of H and N that would have traced either a presolar origin or an irradiation process. Together with the non-detection of the grains in Orgueil, a meteorite rich in presolar grains but depleted in high temperature solar system components (chondrules, Ca-Al-rich inclusions), this suggests that the selective trapping of an anomalous O reservoir by condensation in the early solar system is the most likely origin for the O isotopic anomalies.

References [1] Clayton D.D. and Nittler L.R. (2004) *ARAA* 42, 39-78. [2] Aléon J. et al. (2005) *Nature* in press. [3] Zinner E. et al. (2003) *GCA* 67, 5083-5095. [4] Nguyen A.and Zinner E. (2004) *Science* 303, 1496-1499. [5] Nagashima et al; (2004) *Nature* 428, 921-924. [6] Cami J. and Yamamura I. (2001) *A&A* 367, L1-L4. [7] Aléon et al. (2005) *LPS XXXVI*, Abstract #1901.

FIRST EVIDENCE FOR CO-EXISTING ^{16}O-POOR AND ^{16}O-RICH GASES IN THE EARLY SOLAR NEBULA INFERRED FROM A COMPOUND CA-AL-RICH INCLUSION FROM EFREMOVKA.
J. Aléon[1], A. El Goresy[2] and E. Zinner[3], [1]CRPG-CNRS 15 rue Notre Dame des Pauvres, 54501 Vandoeuvre-les-Nancy, France, aleon@crpg.cnrs-nancy.fr, [2]Bayerisches Geoinstitut, Universität Bayreuth, D-95440, Bayreuth, Germany, [3]Lab. for Space Sciences, Washington University, One Brookings Drive, St. Louis, MO 63130, USA.

Introduction: Compact igneous Ca-Al-rich inclusions (CAIs) in CV chondrites show an oxygen isotope dichotomy: spinel and pyroxene are enriched in ^{16}O, whereas melilite and anorthite are usually not ^{16}O [1]. Recently it was proposed that the ^{16}O-rich composition was the initial composition of the nebular gas [2,3]. However, the origin of the dichotomy is still not well understood. Several mechanisms have been studied involving a late O isotopic exchange with a ^{16}O-poor reservoir during (1) partial melting events [4], (2) solid-state diffusion [5], or (3) parent-body alteration [6] but no single model succeeded in explaining all, observations. Because they have recorded different CAI-forming events, compound inclusions are of great interest and might help in deciphering the origin of these O isotopic variations. E49 is a compound CAI from the reduced CV3 chondrite Efremovka that has previously been studied for mineralogy, petrology, Rare Earth Elements (REE) and Mg isotopes [7]. Both mineralogy and REE patterns indicate that E49 is made of two different lithological units, hereafter called the host and the xenolith, respectively. The host is a fragment of a compact type A inclusion, rimmed by a complete Wark-Lovering sequence (WLR), and consists almost exclusively of melilite, with minor isolated spinel and perovskite grains. The xenolith is mostly composed of spinel and Al-Ti-rich pyroxene, with some melilite and minor anorthite. Fractionated REE patterns in melilite from the host and the xenolith indicate crystallisation from a melt. Melilite from both the host and the xenolith shows ^{26}Mg excesses attributable to the decay of ^{26}Al. The data fall on a single isochron, with an initial ^{26}Al/^{27}Al of 4.1×10^{-5} [7], indicating formation early in the history of the solar system. Oxygen isotopes were measured with the IMS 1270 ion microprobe at CRPG, Nancy, in the two inclusions and the WLR, with an emphasis on melilite.

Results: As typically observed in igneous CAIs, spinel and pyroxene are systematically enriched in ^{16}O (Δ^{17}O < -19 ‰) with one exception in pyroxene. Melilite in the xenolith is rich in ^{16}O with minor variations (Δ^{17}O < -15‰) and has an intermediate composition in the WLR (Δ^{17}O ~ -12‰). In contrast, the oxygen isotopic composition of melilite in the host covers a large range between the ^{16}O-rich spinel and the terrestrial mass fractionation line (-18‰ < Δ^{17}O < +3‰). These variations are correlated with the location within the inclusion. Immediately below the WLR, melilite is ^{16}O-rich, but the ^{16}O-excess decreases progressively toward the center of the inclusion. This variation is correlated with the Åk content of the melilite : ^{16}O-rich melilite below the WLR is nearly pure gehlenite (down to $Åk_1$) and ^{16}O-poor inner melilite is typically $Åk_{20\text{-}30}$. This concentric chemical zonation is typically that observed in melilite from type B1 inclusions [8] and is opposite to that expected from isotopic exchange in a ^{16}O-poor reservoir after CAI crystallisation. This suggests that oxygen isotope exchange took place during crystallisation of melilite from a melt droplet. Two mechanisms can be proposed. (1) The CAI liquid was initially ^{16}O-rich and exchanged O in a ^{16}O-poor reservoir during fractional crystallisation that started from the exterior such as in type B1 CAI mantle [8]. This hypothesis requires diffusion of O from the gas through the compact layer of already crystallised melilite, possibly along melt-wetted grain-boundaries. (2) The host CAI was molten (or partially molten) in a ^{16}O-poor gas but its outer portion later underwent exchange of oxygen in a ^{16}O-rich reservoir. Both hypotheses require rapid transport in nebular regions with different oxygen isotopic compositions. The ^{16}O-rich xenolith was injected into the host melt either in the ^{16}O-poor or ^{16}O-rich reservoir before the onset of fractional crystallization that resulted in the chemical zoning of the host CAI.

Conclusion: Melilite in E49 formed when ^{26}Al was alive. Assuming an initial ^{26}Al/^{27}Al = 7×10^{-5} [9], both a CAI-like ^{16}O-rich and a planetary-like ^{16}O-poor nebular regions were co-existing 5×10^5 years after the birth of our solar system. Oxygen isotopic changes in the protosolar nebula must thus have taken place in less than half a million years.

References: [1] Clayton R.N. et al. (1977) *EPSL* **34**, 209-224. [2] Clayton R.N. (2002) *Nature* **415**, 860-861. [3] Hashizume K. and Chaussidon M. (2005) *Nature* **434**, 619-622. [4] Yurimoto H. et. al. (1998) *Science* **282**, 1874-1877. [5] Ryerson F.K. and McKeegan K.D. (1994) *GCA* **58**, 3713-3734. [6] Wasson J. T. et al. (2001) *GCA* **65**, 4539-4549. [7] El Goresy and Zinner (1994) *Meteoritics*. [8] MacPherson G.J. et al. (1989) *GCA* **53**, 2413-2427. [9] Young E.D. et al. (2005) *Science* **308**, 223-227.

THE REVISED SOLAR ABUNDANCE OF OXYGEN. Carlos Allende Prieto and David L. Lambert, University of Texas, Austin, TX, 78712. callende,dll@astro.as.utexas.edu.

Introduction: Measurements of chemical abundances in the solar photosphere are regularly revised, but tend to change very slowly, in particular for light elements. These changes are usually related to improvements in the available observational material, or the modeling. A few years back, it became apparent that the [OI] line at 630.0 nm, one of the primary indicators of the solar oxygen abundance, was significantly affected by an overlapping Ni I transition. This realization was possible by the use of new 3-D hydrodynamical model atmospheres. Classical 1-D hydrostatic models predict perfectly symmetric line profiles centered at rest wavelengths. Observed line profiles, in turn, are asymmetric and blue-shifted due to convective motions (solar granulation). State-of-the-art solar hydrodynamical models reproduce the observed line profiles with exquisite detail. The observed [OI] feature was suspiciously symmetric and not as blue-shifted as expected, revealing the presence of a contaminating transition.

The forbidden line: The [OI] at 630.0 nm connects the lowest states of the OI atom ($2p\ ^3P$ and $2p\ ^1D$), separated by ~ 2 eV. These levels are thermalized in the solar photosphere and the lines form very close to Local Thermodynamical Equilibrium (LTE) conditions. Line formation calculations in a 3-D hydrodynamical model atmosphere led to a derived abundance 18 % lower than determined from classical static models. A larger correction (see Fig. 1), was due to a blending Ni I feature, further reducing the final abundance estimate by 30 % to $\log \mathrm{N(O)/N(H)} + 12 = 8.69 \pm 0.05$ (Allende Prieto, Lambert & Asplund 2001).

Permitted atomic and molecular transitions: An extension of the analysis based on 3-D model atmospheres to a second forbidden line, permitted O I transitions, and OH molecular lines confirmed the result from the [OI] line at 630.0 nm. Permitted O I lines are formed far from LTE, and therefore detailed 3-D non-LTE calculations are necessary. 3-D effects are significant for molecular species in the presence of convection at solar temperatures, as they tend to concentrate in the cool intergranular lanes. Considering all the indicators, the derived mean value is $\log \mathrm{N(O)/N(H)} + 12 = 8.66 \pm 0.05$ (Asplund et al. 2004). Further support for the revised value was obtained from center-to-limb observations of the OI triplet at 777 nm (Allende Prieto, Asplund & Fabiani Bendicho 2004).

Then, carbon: A slightly smaller correction to the carbon abundance, albeit for somewhat different reasons, was first discovered from an analysis of the [CI] line at 872.7 nm (Allende Prieto, Lambert & Asplund 2002), and later confirmed by a study of C I, CH, and C_2 transitions (Asplund et al. 2005). Compared to previously adopted values, the photospheric abundance was reduced by ~ 30 % to $\log \mathrm{N(O)/N(H)} + 12 = 8.39 \pm 0.05$.

Implications: The revised abundances change the overall solar metallicity (mass fraction of elements heavier than helium) from $Z = 0.017$ to $Z = 0.013$. The new oxygen abundance is in good agreement with measurements in the local interstellar medium for realistic gas-to-dust ratios and the abundances derived for nearby B-type stars, solving a long-standing conundrum. In addition, the reduced Z, has introduced significant problems with helioseismic measurements (Bahcall, Serenelli & Basu 2005). The solution may lie on the opacity calculations for the temperatures relevant at the base of the convection zone (Badnell et al. 2005), or an unexpected value for the Ne abundance in the solar envelope (Antia & Basu 2005). Errors in the surface solar chemical composition dominate the uncertainties in the predicted solar neutrino fluxes (Bahcall & Serenelli 2005).

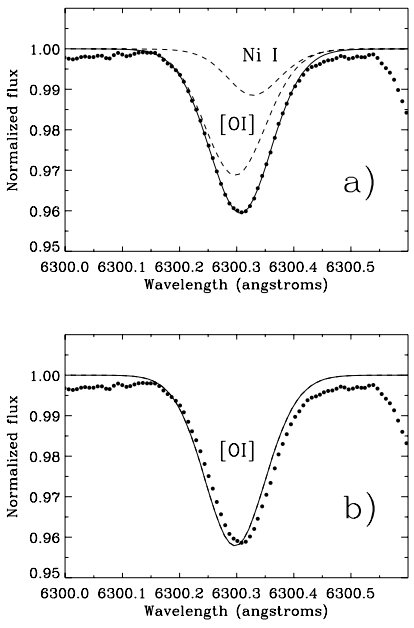


Figure 1: (a) Comparison between the observed (filled circles) and synthetic (solid line) profiles after the χ^2 minimization. The individual calculations of the oxygen and nickel lines are also shown as dashed lines. (b) Best fit, assuming the observed feature is entirely produced by the oxygen forbidden line.

OXYGEN ISOTOPES IN THE VOLATILE MATERIAL OF COMETS

K. Altwegg, H. Balsiger, Physikalisches Institut, University of Bern, Sidlerstr. 12, CH-3012 Bern, Switzerland, altwegg@phim.unibe.ch

The material of comets represents the most pristine material to be found in the solar system. Studying the composition of this material can help to understand the history of the solar system formation and can connect the present day composition of the solar system with the composition of the molecular cloud from which it emerged. Isotopic ratios are one of the most important clues for the chemical and physical processing of the material since its formation.

In the talk we will review the measurements of the oxygen isotopic ratio in the volatile material of comets. We will discuss the possible fractionation processes in the formation of the molecules. Because most measurements have been and will also in the future be made in the coma of comets it is important also to know possible fractionation processes in the nucleus, during sublimation and in the coma.

Rosetta on its way to 67P/Churyumov-Gerasimenko will be the first spacecraft which can analyze oxygen isotopes in situ in different molecules (e.g. CO, CO2) on a cometary surface [1]. It will also measure deuterium, oxygen isotopes, and other isotopes in different molecules of the cometary coma [2]. The capabilities of the corresponding instruments will be discussed.

For the correct interpretation of the data we will need relevant laboratory measurements of reaction rates and processes. A list of such measurements will be presented

References:

[1] I. P. Wright, and C. T.Pillinger (1998) *Adv. Space Res. 21*, 1537–1545. [2] H. Balsiger, K. Altwegg, E. Arijs, J.-L. Bertaux, J.-J. Berthelier, B. Block, P. Bochsler, G.R. Carignan, L. Duvet, P. Eberhardt, B. Fiethe, J. Fischer, L.A. Fisk, S.A. Fuselier[7], A.G. Ghielmetti[7], F. Gliem[6], T.I. Gombosi[9], M. Illiano[3], T. Koch[1], E. Kopp, A. Korth, K. Lange, H. Lauche, S. Livi, A. Loose, T. Magoncelli, C. Mazelle, M. Mildner, E. Neefs, D. Nevejans, H. Rème, J. A. Sauvaud, S. Scherer, A. Schoenemann, E.G. Shelley, J. H. Waite, C. Westermann, B. Wilken, J. Woch, H. Wollnik, P. Wurz, D.T. Young, ESA-SP 1165, 2001, in print

High Energy Radiation Fields Impinging the Surfaces of Protoplanetary Disks

Edwin A. Bergin Dept. of Astronomy, University of Michigan, Ann Arbor MI 48109

In recent years there has been new information gleaned on the shape and strength of the far-ultraviolet (FUV) radiation field that characterizes the early stages of proto-stellar evolution. I will present these new observations and examine the nature of this field and show that there is clear evidence for a dominant flux in hydrogen Lyman alpha that induces molecular hydrogen fluorescence and an additional source of FUV continuum that may be induced by stellar X-rays. Energetic radiation and an evolving dust opacity (due to coagulation and sedimentation) are key determinants of the disk chemical evolution. I will show how these various factors influence the chemistry, with a focus on water, a key oxygen bearing species.

STATUS OF OXYGEN ISOTOPE MEASUREMENTS FROM GENESIS SOLAR WIND SAMPLES. D. S. Burnett and the Genesis Science Team, Division of Geological and Planetary Sciences, 100-23, California Institute of Technology, Pasadena, CA 91125 (burnett@gps.caltech.edu).

Background The Genesis Discovery Mission exposed pure materials to the solar wind at the L1 Lagrangian Point for 27 months from December 2001 through March 2004 [1]. In mission planning, we identified 19 prioritized "measurement objectives", i.e., specific studies related to various aspects of solar abundances. The first 6 of these were isotopic studies and the highest priority was assigned to the measurement of the oxygen isotopic composition.

In addition to passive collectors, LANL science team members designed an ion telescope ("Concentrator"), which focused the solar wind by about a factor of 20 onto a 6 cm diameter "target" [2,3]. The Concentrator was built essentially entirely to support oxygen isotopic analysis because of the ubiquity of oxygen as a contaminant in potential collector materials, and as background in potential analytical schemes.

A parachute deployment failure caused the crash of the Sample Return Capsule upon return to Earth. This has caused damage and contamination of the collector materials. However, we have recovered sufficient quantities of materials to meet our science objectives. We have not yet demonstrated that we can adequately decontaminate the samples for all analyses, but a wide variety of promising approaches are being tested. We are cautiously optimistic that we can accomplish most of our measurement objectives.

Materials for Oxygen Isotopic Analysis. The Concentrator target is divided into four 3 cm radius quadrants. Two of the quadrants are epitaxially grown single crystal SiC (CREE, Inc). One quadrant is polycrystalline CVD diamond made from 99% isotopically pure ^{13}C (Raytheon, Inc.). The final quadrant is an amorphous diamond-like carbon layer on silicon prepared by T. Friedmann (Sandia Labs). All three materials have been shown to be sufficiently pure. Among the passive collectors, float zone silicon is sufficiently pure for oxygen isotope analysis.

Status. The Concentrator target was recovered intact after the crash with 3 of the 4 targets in place. The Sandia quadrant was broken into several pieces, but these have been recovered. Visual inspection indicates no major surface damage.

Analysis Plans. A Genesis Allocation Committee is in place (A. M. Davis, Chair) and sample request guidelines are available (judith.h.allton@jsc.nasa.gov). Samples are available to all qualified analysts.

A major advantage of sample return missions is that important measurements can be replicated using different analytical approaches. In this spirit, the Project has supported 3 analytical approaches and selected appropriate materials: (a) high energy SIMS analysis (K. D. McKeegan, UCLA); (b) laser ablation of the ^{13}C CVD diamond with analysis by static source gas mass spectrometry as CO (I. Franchi, Open U.); and (c) laser fluorination with analysis as O_2 (M. H. Thiemens, UCSD).

Precision. The required precision for oxygen isotopic analysis was initially set as ± 1 ‰, 2 σfor both ^{17}O and ^{18}O. Eventually, a measurement to at least this precision is highly desirable. However, since important differentiation between present models for the origins of oxygen isotopic variations in planetary materials can be made with lower precision than this, the Allocation Committee is prepared to support a request for an initial measurement with lower precision than 1 ‰.

References. [1] D. S. Burnett et al. (2003) *Space Sci. Rev., 105*, 509. [2] J. E. Nordholt et al. (2003) *Space Sci. Rev., 105*, 561. [3] R. C. Wiens et al. (2003) *Space Sci. Rev., 105*, 601.

OXYGEN ISOTOPES OF SECONDARY PHASES IN UNEQUILIBRATED CHONDRITES: IMPLICATION FOR THE FLUIDS/ICES IN THE NEBULA AND ASTEROIDS. B.-G. Choi[1], M. Cosarinsky[2] and J. T. Wasson[2], [1] Earth Science Education, Seoul National University, Seoul 151-748 KOREA (bchoi@snu.ac.kr), [2]Earth and Space Sciences, University of California, Los Angeles, CA90095-1567, USA.

Chondrites are mixtures of materials that formed at many different times, places and conditions in the solar nebula and asteroids. Thus the O isotope heterogeneity recorded in them must be interpreted as a result of such events. The O isotopes of high-temperature solar nebular gas are recorded in refractory phases in chondrites, such as pristine CAIs and chondrules. However, many of them, even in the most primitive chondrites, experienced various degrees of alteration in the nebula or, more significantly, in their parent bodies. Therefore, the secondary signature must be extracted to sort out the primary oxygen. The secondary oxygen can be measured or estimated from secondary and altered phases. In addition, the compositions of such oxygen give the information on the nature of the fluid present in chondritic asteroids and of low-temperature nebular gas that condensed either as OH in hydrous silicates or ice in inner or outer solar system, respectively.

The $\Delta^{17}O$ values of hydroxyl in phyllosilicates [1,2], calcites [3] and magnetite [4-9] from unequilibrated chondrites are shown in Fig. 1, along with those of matrix and whole rocks [10,11].

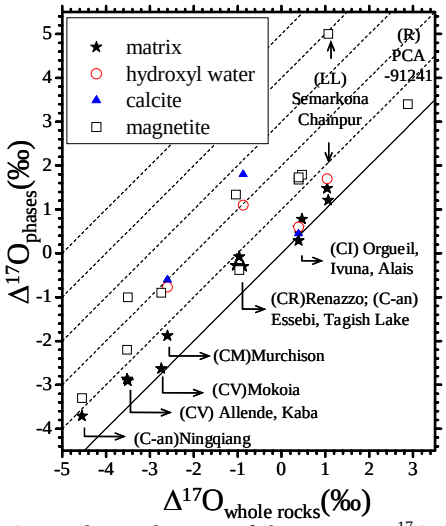


Fig. 1. A correlation diagram of the average $\Delta^{17}O$ values of secondary phases *vs.* their host chondrites. The solid line is for $\Delta^{17}O_{phases} = \Delta^{17}O_{whole\ rock}$ and the dashed lines for $\Delta^{17}O_{phases} = \Delta^{17}O_{whole\ rock} + 1, +2, +3, +4, +5$.

Some anhydrous silicates in chondrites seem to have been affected by aqueous alteration. The $\Delta^{17}O$ of melilite is about -4‰ in most carbonaceous chondrite CAIs. Efforts to account for this by exchange with the nebular gas have not been successful. It was shown that melilite in unaltered carbonaceous chondrites has $\Delta^{17}O$ <-20‰ and suggested that melilite in altered chondrites exchanged by asteroidal alteration [12]. In CVs olivines of matrix and accretionary rims show continuous mixing between primary ^{16}O-rich and secondary ^{16}O-poor oxygen. This progressive variation correlates with FeO content [13]. In contrast, altered products, mostly Ca- and Fe-rich silicates, define a mass fractionation line with a $\Delta^{17}O$ of -3 to -2 ‰ [14].

The O isotopes of asteroidal water can be estimated by measuring OH in phyllosilicates. The $\Delta^{17}O$ values of water released by pyrolysis are up to 2‰ higher than whole rocks. It should be noted that this hydroxyl water is probably not the original water that altered chondrites, instead it is secondary after isotopic exchange with other phases during alteration.

The $\Delta^{17}O$ values of calcite are also up to 2 or 3 ‰ higher than those of whole rocks. In CMs, carbonates show variable $\Delta^{17}O$, which correlate with degree of alteration, possibly means different water/rock ratios.

In unequilibrated chondrites magnetite has the highest $\Delta^{17}O$ values, with large variations in both $\delta^{18}O$ and $\Delta^{17}O$ even in a single chondrite. Along with petrological characteristics, this imply that magnetite formed by reaction between O-free phases and fluid in closed systems. The larger the O isotopic variations and differences between magnetite and whole rocks are, the smaller the O isotopic exchange between fluid and rocks prior to magnetite formation.

In summary, (1) the $\Delta^{17}O$ values of secondary and altered phases are always larger than those of whole rocks and 'primary phases', (2) in most unequilibrated chondrites, magnetite has the highest $\Delta^{17}O$ followed by calcite and hydroxyl water. (3) The $\Delta^{17}O$ values of initial water for carbonaceous and ordinary chondrite parent asteroids were > 2 and > 7‰, respectively, and became progressively smaller during aqueous alteration, and (4) during the condensation of water the $\Delta^{17}O$ values of the nebular gas were larger than 7‰.

References: [1] Robert F. et al. (1979) *Nature, 282,* 785-789. [2] Baker L. et al. (2002) *Meteoritics & Planet. Sci., 37,* 977-985. [3] Benedix B.K. et al. (2003) *GCA, 67,* 1577-1588 [4] Rowe M.W. et al. (1994) *GCA, 58,* 5344-5347. [5] Choi B.-G.et al. (1997) *EPSL 146,* 337–349. [6] Choi B.-G. et al. (1998) *Nature 392,* 577-579. [7] Choi B.-G. et al. (2000) *Meteorit. Planet. Sci 35,* 1239-1248. [8] Greenwood P.J. et al. (2000) *GCA, 64,* 3897-3911. [9] Choi B.-G & Wasson J.T. (2003) *GCA, 67,* 4655-4660. [10] Clayton R.N. et al. (1991) *GCA, 55,* 2317-2339. [11] Clayton R.N. & Mayeda T.K. (1999) *GCA, 62,* 2089-2104. [12] Wasson J.T et al. (2001) *GCA, 65,* 4539-4549. [13] Cosarinsky M. et al. (2002) *Meteoritics & Planet. Sci., 37,* A38. [14] Cosarinsky M. et al. (2003) *LPS, 34,* #1043.

ASTROPHYSICAL MODELING OF THE DISTRIBUTION OF WATER IN PROTOPLANETARY DISKS: IMPLICATIONS FOR NEBULAR REDOX CONDITIONS AND OXYGEN ISOTOPES. F. J. Ciesla,[1] A. N. Krot[2], and M. I. Petaev[3], [1]NASA Ames Research Center, MS 245-3, Moffett Field, CA 94035, ciesla@cosmic.arc.nasa.gov, [2]Hawai'i Institute of Geophysics and Planetology, University of Hawai'i at Manoa, Honolulu, Hawai'i 96822, sasha@higp.hawaii.edu, [3]Harvard-Smithsonian Center for Astrophysics and Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138, mpetaev@cfa.harvard.edu.

Introduction: Protoplanetary disks are evolving objects. Observations show that mass is transferred through these objects and accreted by the central star at rates up to 10^{-6} solar masses per year and decreasing over time [1]. This evolution is observed to last up to ~10 million years in some systems and results in the disks cooling and becoming less massive over time. Superimposed on this evolution will be the transport of solids and gaseous molecules by advection, diffusion, and gas drag migration. These processes will combine to change the physical and chemical structure of the disks over their lifetimes. It is in this context that we must understand how early solar system solids were processed.

Absolute and relative chronologies of chondrules and refractory inclusions in primitive chondrites provide important constraints on the duration of thermal processing of solids in our protoplanetary disk. Pb-Pb [2,3] and Al-Mg isotopic studies [5] show that CAI formation started 4567.2±0.7 Myr ago and may have lasted < 0.5 Myr; chondrule formation may have started shortly after CAIs and lasted for ~3 Myr. Although chondrules in CB chondrites formed 4562.7±0.6 Myr ago, they appear to have formed by a collision between planetary embryos after dust in the protoplanetary disk largely dissipated [6]. Based on these observations, we infer that our protoplanetary disk may have lasted $\leq$ 3-5 Myr.

The mineralogy and O-isotopic compositions of CAIs, AOAs, and chondrules recorded redox conditions and O-isotopic compositions of the inner solar nebula. CAIs and AOAs appear to have formed in an ^{16}O-rich nebular gas under relatively reduced conditions. In contrast, most chondrules originated in the presence of ^{16}O-por nebular gas under oxidizing conditions (chondrules in enstatite chondrites are the only exception) [e.g., 6,7]. We will discuss a physical model that can explain this meteoritic record in a way that is consistent with astronomical observations.

Model: We have recently developed a model to track how the distribution of water changes in an evolving protoplanetary disk [8]. The disk evolution is calculated using the α-viscosity model where the viscosity is assumed to be due to turbulence in the disk. This allows us to calculate how the surface density and temperature structure change over the disk lifetime.

As the disk evolves, we also track how the water distribution changes as the vapor and solids are subjected to transport, vaporization, condensation, accretion, and collisional destruction. We consider four distinct dynamic groups of nebular materials: vapor, dust, migrators, and planetesimals. Vapor and dust will be transported by diffusion, which carries them either inward or outward along concentration gradients. Migrators correspond to the meter-sized rubble in the disk that is rapidly carried inward (~1 AU/century) by gas drag. Planetesimals are larger objects (>1 km) which are massive enough to be unaffected by the gas in the disk and are immobile in our simulations.

Results: In the early stages of disk evolution, water transport is dominated by the coagulation of dust particles into meter-sized rubble that then rapidly moves inwards due to gas drag. This results in more water being carried inward across the snow line than can be removed by the advection of the disk and diffusion of water vapor. Thus the inner disk immediately inside the snow line becomes enhanced in water vapor. This inward flux continues as the water vapor is redistributed in the inner disk, resulting in a uniform enhancement of water vapor inside of the snow line, with the maximum enhancement reaching ~10×solar. These inward migrating bodies may be enriched with heavy oxygen isotopes, causing the inner disk to become increasingly ^{16}O poor over time, which is consistent with O-isotopic evolution of the inner solar nebula recorded by chondrules and refractory inclusions [6, 8-11].

Over time the influx of icy bodies from the outer disk diminishes for two reasons. The first is that as migrators form and are carried inwards over time, the outer disk becomes depleted in dust and is no longer able to readily create these fast moving objects. The second reason is that as planetesimals grow in the outer disk, it becomes more likely that the migrators would be swept up and accreted rather than surviving their transport to the inner disk. Because vapor is not being supplied to the inner disk at such a rapid rate, diffusion becomes the dominant transport mechanism. Vapor is thus carried outward where it condenses and the resulting solids are then locked up in the planetesimals in the outer disk. The concentration of vapor in the inner disk then decreases over time.

Discussion: The evolution of protoplanetary disks naturally leads to fluctuating oxidation conditions inside the snow line. The environment that forms inside the snow line is intimately tied to processes (both physical and chemical) that occur in the outer disk. We will discuss how this evolution can explain the observations of the oxidation state and O-isotopic compositions of materials in primitive meteorites.

References: [1] Calvet N. et al. (2005) *AJ, 129,* 935-946. [2] Amelin Y. et l. (2002) *Science, 297,* 1678-1683. [3] Amelin Y. et al. (2004) *GCA, 68,* A759. [4] Bizzarro M. et al. (2004) *Nature, 431,* 275-278. [5] Krot A. N. et al. (2005) *Nature,* in press. [6] Krot A. N. et al. (2002) *Science, 295,* 1051-1054. [7] Krot A. N. et al. (2000) in *Protostars and Planets IV,* eds. Boss A., Manning V., and Russell S., Arizona Press, 1019-1054. [8] Ciesla F. J. and Cuzzi J. N. (2005) *Icarus,* submitted. [9] Yurimoto H. and Kuramoto K. (2004) *Science, 305,* 1763-1766. [10] Krot A. et al. (2005) *ApJ, 622,* 1333-1342.. [11] Lyons J. R. and Young E. D. (2005) *Nature, 43,5,* 317-320.

HISTORICAL PERSPECTIVE — THE UNIQUE ROLE OF OXYGEN IN THE EARLIEST SOLAR SYSTEM. Robert N. Clayton, Enrico Fermi Institute, University of Chicago, Chicago, IL 60637 (r-clayton@uchicago.edu).

The modern era of oxygen isotope cosmochemistry began in 1969, the year of the fall of the Allende carbonaceous chondrite, and of the first lunar sample return. The "fingerprint" or provenance applications were not known at that time, and the emphasis was on thermometry, identifying the igneous origins of differentiated achondrites and lunar rocks, the conditions of metamorphism of ordinary chondrites, and the low-temperature aqueous alteration of CI and CM chondrites. Complications arose in the attempt to use $^{18}O/^{16}O$ ratios in Allende CAIs to estimate their condensation temperature. The entire nature of the subject changed in 1973 with the accidental discovery of variations in $^{17}O/^{16}O$ that did not follow the expected mass-dependent fractionation law. It was quickly recognized that the array on a three-isotope graph represented some sort of two-component mixing line, with end-members differing primarily in their abundance of ^{16}O. The nature and origins of these reservoirs was an unsolved question for the next thirty years, in part because there were two alternative reasonable interpretations: (1) an inherited isotopic heterogeneity of the solar nebula, of nucleosynthetic origin, and (2) an isotopic heterogeneity produced *within* the nebula by a non-mass-dependent chemical reaction. A third mechanism, based on isotope-selective photolysis of carbon monoxide, was discussed in the context of molecular clouds in the astronomical literature since 1972 [1, 2], but was largely ignored by the meteoritical community. Photochemical shielding in O_2 was considered as a possible solar nebular process [3, 4], but was abandoned [5] when it was shown that the non-mass-dependent fractionation in ozone formation does not require photolysis of O_2.

Several elements (H, C, N, O, and noble gases) are strongly depleted in solid planetary bodies, so that their isotopic compositions in those bodies need not be representative of the overall solar nebula, now represented by the Sun. The solar isotopic compositions of most of these elements are unknown, but should soon be revealed through laboratory analyses of the Genesis solar wind samples. Without knowledge of the solar composition, it has been difficult to interpret isotopic analyses of these elements in meteorites and planets. One advantage of the photochemical shielding model is that it makes a specific prediction of the solar oxygen isotope composition, and is therefore falsifiable. The same is not true for alternative models.

Three alternative versions of the self-shielding model have been proposed, differing in the astrophysical setting, which leads to large differences in gas densities, temperatures, and time-scales. All of these models predict that the mean oxygen isotopic composition of the solar nebula, and hence the present-day composition of the Sun, is quite different from that of the Earth and other inner solar system solid bodies, and is probably close to that seen in the ^{16}O-rich end of the CAI mixing line, at $\delta^{17}O = \delta^{18}O \approx -50‰$. The models of Yurimoto and Kuramoto [6] and Lyons and Young [7] use photolysis of CO at low densities and low temperatures to form ^{16}O-depleted atomic oxygen, which reacts with hydrogen to form water ice, [6] in the parent molecular cloud or [7] in the outer reaches of the solar nebula. This ^{16}O-poor water reservoir subsequently reacts with solar-composition solids, in a separate process, to generate the slope-1 mixing line seen in meteorites. Time-scales for production of the ^{16}O-poor water reservoir, using ambient starlight as the source of ultraviolet radiation, are on the order of 10^5 years [6, 7]. The third model [8, 9] envisions the photochemical isotope effect and the formation of chondrules and CAIs as parts of the same process, occurring very near the growing Sun, on time-scales of seconds to days. These conditions are met in the X-wind models of Shu and others [10]. The advantage of the X-wind setting is that it unites the chemical and isotopic aspects of oxygen in the earliest solar system.

References. [1] Bally J. and Langer W.D. (1982) *Astrophys. Jour.* **255**, 143–148. [2] van Dishoeck E.F. and Black J.H. (1988) *Astrophys. Jour.* **334**, 771–802. [3] Thiemens M.H. and Heidenriech J.E. (1983) *Science* **219**, 1073–1075. [4] Kitamura Y. and Shimizu M. (1983) *Moon and Planets* **29**, 199–202. [5] Thiemens M.H. (1996) in *Chondrules and the Protoplanetary Disk*, R.H. Hewins, R.H. Jones, and E.R.D. Scott, eds. (Cambridge). [6] Yurimoto H. and Kuramoto K. (2004) *Science* **305**, 1763–1766. [7] Lyons J.R. and Young E.D. (2005) *Nature* **435**, 317–320. [8] Clayton R.N. (2002) *Nature* **415**, 860–861. [9] Clayton R.N. (2005) *LSPSC XXXVI*, #1711 pdf. [10] Shu F.H., Shang H., and Lee T. (1996) *Science* **271**, 1545-1552.

EXPERIMENTAL CONSTRAINTS ON HIGH TEMPERATURE OXYGEN ISOTOPIC EXCHANGE AND ON MASS DEPENDENT ISOTOPIC FRACTIONATION AND REDOX CONDITIONS DURING EVAPORATION. A. M. Davis[1] and K. D. McKeegan[2], [1]Enrico Fermi Inst., Dept. of Geophysical Sciences, and Chicago Center for Cosmochemistry, University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637 (a-davis@uchicago.edu), [2]Dept. of Earth and Space Sciences, University of California, Los Angeles, CA 90095 (mckeegan@ess.ucla.edu).

Introduction: Calcium-, aluminum-rich inclusions (CAIs) in primitive meteorites provide a record of thermal and chemical processing in the early solar system. Here we review experimental measurements of self-diffusion of oxygen in minerals and of the isotopic and redox effects of high temperature evaporation.

Diffusion of Oxygen: After the discovery of ^{16}O excesses in CAIs [1], Clayton and coworkers investigated the effect in more detail by analyzing mineral separates from a number of individual CAIs [2]. In addition to defining the now well-known slope-0.95 CCAM (carbonaceous chondrite anhydrous material) line on the three-isotope oxygen plot, they made a remarkable discovery: regardless of which CAI was analyzed, different minerals cluster at different positions along the CCAM line. It is convenient at this point to introduce the quantity $\Delta^{17}O$, which provides a measure of deviation from the terrestrial mass fractionation line and is defined as $\delta^{17}O - 0.52 \times \delta^{18}O$. Spinel is quite ^{16}O-rich, with $\Delta^{17}O = -20$ ‰ and fassaitic pyroxene is nearly as ^{16}O-rich, with $\Delta^{17}O = -15$ to –20 ‰. In contrast, melilite and anorthite lie close to the terrestrial fractionation line, with $\Delta^{17}O = -6$ to –2 ‰. This result was quite striking, as crystallization of a CAI from a melt is expected to yield minerals that all have the same $\Delta^{17}O$ value. A number of explanations were proposed, among them that all minerals initially crystallized with $\Delta^{17}O \approx -20$ ‰ and were then later exchanged with another reservoir with $\Delta^{17}O \approx 0$ ‰. This required that melilite have a much faster diffusion rate for oxygen than pyroxene and spinel, but no measurements of relevant diffusion rates were available at the time.

The first reliable measurements of self-diffusion of oxygen in melilite came in 1989 [3], with the use of an ion microprobe to measure diffusion profiles in single crystals of åkermanite and gehlenite from diffusion experiments. Diffusion rates for åkermanite are about ten times faster than for gehlenite along the same crystallographic direction and in åkermanite, diffusion is about ten times faster along the *a*-axis than along the *c*-axis. The most useful set of oxygen self-diffusion coefficients were obtained by ion microprobe depth profiling in natural diopsidic pyroxenes, natural anorthite, synthetic spinel and synthetic åkermanite [4]. Models with isothermal heating or linear cooling showed that if the observed grain sizes are used for the diffusion dimensions, the observed data in CAIs were not reproduced; a better match was obtained by making the domain sizes of anorthite, pyroxene and spinel the same [4]. Partial melting and solidification provided the best fit for melilite, anorthite and spinel, but this model predicted that pyroxene would have the same isotopic composition as melilite. The failure of these simple models led to the conclusion that processes other than diffusion and partial melting must play a role in oxygen isotopic exchange [4].

Diffusive exchange remains a possibility, as the order of increasing diffusion coefficients and $\Delta^{17}O$ in CAI minerals are: spinel, pyroxene, anorthite, melilite.

Oxygen Isotopic Effects of Evaporation: A class of CAIs with oxygen isotopic compositions off the CCAM line, the FUN (for their Fractionation and Unidentified Nuclear isotopic effects) inclusions were discovered in 1977 [5]. It seems that these CAIs may have begun with the same oxygen isotopic composition as normal CAIs, on the CCAM line with $\Delta^{17}O = -20$ ‰. They were then mass fractionated along a line parallel to the terrestrial fractionation line and subsequently partially exchanged oxygen with the same reservoir as the normal CAIs. The idea that the large isotopic fractionation effects in oxygen could be produced by high temperature evaporation was confirmed experimentally in vacuum evaporation of Mg_2SiO_4 melts [6]. Oxygen isotopes followed the predicted Rayleigh behavior for fractionation by the kinetic isotope effect, but the fractionation factor was somewhat smaller than predicted. Subsequent vacuum evaporation experiments on melts of initially chondritic composition showed similar effects [7].

Redox Effects of Evaporation: Evaporation is a kinetic process, so that equilibrium terms such as oxygen fugacity are not applicable. Nonetheless, evaporation residues can have interesting redox effects. Vacuum evaporation of rare-earth-doped chondritic melts [7] or of bulk Allende meteorite [8] produced large negative cerium anomalies in residues, suggesting highly oxidizing conditions. These anomalies are not observed in vacuum experiments run in much more reducing conditions, in low-pressure hydrogen [9]. There can also be indicators of both oxidizing and reducing conditions in the same experiment. Vacuum evaporation of REE-doped stoichiometric perovskite produced negative cerium anomalies, indicating oxidizing conditions [10], but the residue quenches to perovskite plus a titanium oxide in which about half of the titanium is trivalent and half tetravalent, indicating reducing conditions [11].

References: [1] Clayton R. N. et al. (1973) *Science, 182*, 485. [2] Clayton R. N. et al. (1977) *EPSL, 34*, 209. [3] Yurimoto H. et al. (1989) *GCA, 53*, 2387. [4] Ryerson F. J. and McKeegan K. D. (1994) *GCA, 58*, 3713. [5] Clayton R. N. and Mayeda T. K. (1977) *GRL, 4*, 295. [6] Davis et al. (1990) *Nature, 347*, 655. [7] Wang J. et al. (2001) *GCA, 65*, 479. [8] Floss C. et al. (1996) *GCA, 60*, 1975. [9] Davis A. M. et al. (1999) *LPS XXX*, Abstract #2023. [10] Davis A. M. and Hashimoto A. (1995) *Meteoritics, 30*, 500. [11] Davis A. M. et al. (1995) *LPS XXVI*, 317.

Astronomical and Spectroscopic Perspective of Comets: Direct Detection of Oxygen-bearing Parent Volatiles at Infrared Wavelengths

M. A. DiSanti[1] and N. Dello Russo[2], [1]Solar System Exploration Division, Code 693, NASA-Goddard Space Flight Center, Greenbelt, MD 20771, disanti@ssedmail.gsfc.nasa.gov, [2]Space Department, JHU/APL, Neil.Dello.Russo@jhuapl.edu

The near infrared ($\lambda \sim 2.5 - 5.0$ μm) is ideal for the study of molecules housed as ices in the nuclei of comets ("parent" volatiles), as this spectral region contains a multitude of ro-vibrational bands. Over the past decade, it has become possible to conduct direct ground-based measurements of important constituent molecules using modern long-slit array spectrometers. These instruments (NIRSPEC at Keck 2 10-m telescope and CSHELL at the NASA-IRTF 3-m telescope, both located atop Mauna Kea, HI) provide high spectral resolving power ($\lambda/\Delta\lambda \sim 2 - 3 \times 10^4$) and small pixels, thereby permitting line-by-line study of the spatial distribution of emission intensities along the slit.

Since 1996, our group has routinely measured up to ten parent molecules in comets, using CSHELL and NIRSPEC. Included are carbon monoxide (CO) and methyl alcohol (CH_3OH) in all eleven Oort cloud comets observed, and formaldehyde (H_2CO) in six of these (C/1999 H1 Lee, C/2001 LINEAR A2, C/2001 LINEAR WM1, C/2002 C1 Ikeya-Zhang, C/2002 LINEAR T7, and C/2004 Q2 Machholz). In each comet observed, we also have simultaneous direct measurements of H_2O, the most abundant ice in comets, through non-resonant fluorescent emission and/or prompt emission from OH, which we use as a proxy for the parent H_2O.

Measuring the abundances of the chemically-linked molecules CO, H_2CO, and CH_3OH in comets can provide a test of the efficiency of conversion of CO, for example through surface hydrogen addition on the icy mantles of pre-cometary grains, or by radiation processing in the dense cloud core. The conversion efficiency is expected to depend on local H-atom densities, and laboratory measurements suggest a strong dependence on temperature between ~10 and 25 K as well. Therefore, its measurement can provide information on conditions to which the grains were exposed prior to their incorporation into the nucleus.

Accurate abundance measurements require knowledge of the excitation state of molecules in the coma (i.e., knowledge of the rotational temperature, T_{rot}). We will present comparisons between modeled and observed emission intensities. These comparisons are based on two complementary approaches: (1) A correlation analysis between the observed emission spectrum containing lines spanning a range in rotational energy and the modeled spectrum convolved to the resolution of the data. The best-fit value of T_{rot} corresponds to the maximum correlation coefficient. (2) A Boltzmann (excitation) analysis, where the ratio of observed to predicted line strengths is plotted against rotational energy for states giving rise to each line. At the best-fit T_{rot}, this ratio is independent of energy (i.e., the least-squares slope is zero).

Having accurate abundances for H_2O, CO, H_2CO, and CH_3OH permits robust mixing ratios (abundances relative to H_2O) in the nucleus to be determined. Based on these, conversion efficiencies for CO will be presented for several comets in our database, and comparisons will be made with laboratory measurements.

This work was supported by NASA grants RTOP 344-33-55, 344-32-98, and 344-32-30-07, plus NNG05GA64G.

EVOLUTION OF OXYGEN ISOTOPIC COMPOSITION AND C/O RATIO AT LATE STAGE OF PROTO-PLANETARY ACCRETION DISK. T. Fukui and K. Kuramoto, *Hokkaido University, Sapporo 060-0810, Japan, (ftakashi@ep.sci.hokudai.ac.jp).*

Introduction: It is well known that chondrites have following chemical/isotopic features: (i) Their constituents show mass-independent fractionation of oxygen isotopic composition. In particular, CAIs have ^{16}O-rich composition, and chondrules have ^{16}O-poor one. (ii) Redox state of chondritic groups is different from each other. In addition, more reduced group tends to have higher Si/Mg ratio. This relation is well explained by inhomogeneous addition of reduced material SiC [1]. However, reduced environment (C/O $>$ 0.95) is required for SiC formation [2]. These features imply that isotopic and chemical compositions of proto-planetary disk considerably changed with time and location. In this study, we simulate the chemical and isotopic evolution of a proto-planetary disk.

Mechanisms which control composition of disk: In a proto-planetary accretion disk, dust particles migrate inward faster than gas due to gas drag. Their migration velocities strongly depend on the mass accretion rate and the velocity ratio of dust to gas (v_{dust}/v_{gas}) increases with the decay of accretion. Volatile components in dust particles evaporate when ambient temperature exceeds their frost point. The difference in migration velocity between dust and gas causes enrichment of dust evaporants in gas phase. In this way, the composition of inner disk deviates from the original (solar) one.

Icy and organic materials play important role in changing isotopic and redox condition in the inner disk. In molecular cloud, H_2O ice is expected to be ^{16}O-poor and CO gas to be ^{16}O-rich [3]. H_2O enrichment caused by the above process would change O isotopic composition of inner disk in ^{16}O-poor direction. In a similar way, evolution of C/O ratio would change by the enrichment of H_2O ice and organic evaporants.

We perform numerical calculation to estimate the effect of these processes quantitatively and examine how the oxygen isotopic composition and C/O ratio could evolve in a proto-planetary accretion disk.

Numerical model: The concentrations of dust evaporants are described by advective-diffusive equations

$$\frac{\partial c_i}{\partial t} + v_r \frac{\partial c_i}{\partial r} - \frac{1}{\Sigma r}\frac{\partial}{\partial r}\left(\Sigma r D \frac{\partial c_i}{\partial r}\right) = \frac{S_i}{\Sigma}, \qquad (1)$$

where c_i is the concentration of dust species i in the disk with the gas accretion velocity v_r, the surface density Σ and the diffusion coefficient D. S_i is the source of species i due to evaporation. Our reference model assumes steady temperature and surface density profiles same as the "minimum mass" solar nebula model [4]. In this model, H_2O ice and organic material evaporate at 3, 0.3 AU from the disk center, respectively. Under these conditions, we perform numerical calculations for the case that mass accretion rate decreases from 10^{-8} to $10^{-9} M_\odot$/yr, which are typical for the late stage of proto-planetary accretion disk [5].

Results & Discussion: As the accretion rate decreases H_2O and C-bearing vapor begin to concentrate from their evaporation fronts respectively and are transported inward by gas accretion (Fig. 1A). This is caused by the increase in v_{dust}/v_{gas} with the decay of disk accretion. The H_2O enrichment in gas phase makes O isotopic composition of the disk center gradually ^{16}O-poor (Fig. 1B). Increase in $\delta^{17,18}$O (+70 ‰) caused by these processes is large enough to explain that of meteorites (+50 ‰) relative to ^{16}O-rich CAI. C/O ratio of the disk also changes with the enrichment of H_2O and C-bearing vapor (Fig. 1C). If these evaporants are mixed in their original relative fraction, the C/O ratio will be almost kept at the solar proportion. However, water vapor which evaporate at 3 AU takes some time to be transported to the disk center. This time lag nearly equals the regidence time of inner disk given by $M_D/\dot{M}_D \sim 4 \times 10^6$ yr. When the time scale of the accretion decay is much shorter than the regidence time, the C/O ratio of the disk center will considerably change. The condition required for SiC formation would be satisfied during 1/3 of the residence time. Thus sufficient amount of SiC would be formed and possibly affect the redox state of the inner disk if they are returned to disk by some sort of material circulation.

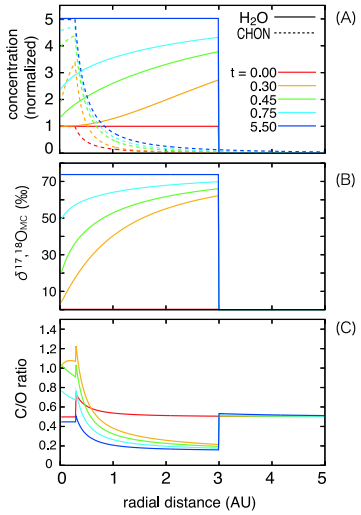


Figure 1: (A) Concentration profiles of H_2O and C-bearing vapor in gas phase. The concentrations are normalized by which achieved for unfractionated solar nebula. Time is scaled by residence time of the inner disk. In this case, we assumed accretion rate instantaneously decreases. The lower panels show the time variation of O isotopic composition (B) and C/O ratio (C). In this case, $\delta^{17,18}$O of H_2O ice and CO gas are $+100$‰, -230‰, respectively. For the original mixture of gas and dust, C/O ratio is taken to be 0.5, a half of C is partitioned to CO gas and another half to be organic materials. O is partitioned into silicate, H_2O and CO to be 1:3.5:1.5.

References: [1] Kuramoto, K. and Yurimoto, H. (2005) in "*Chondrites and Protoplanetary Disk*", edited by Krot, A. N. et al., 181. [2] Krot, A. N. et al. (2000) in "*Protostars and Planets IV*", edited by Mannings, V. et al., 1019. [3] Yurimoto, H. and Kuramoto, K. (2004) *Science* 305, 1763. [4] Hayashi, C. et al., (1985) in "*Protostars and Planets II*", edited by Black, D. C., Matthews, M. S., 1100. [5] Calvet, N. et al., (2000) in "*Protostars and Planets IV*", edited by Mannings, V. et al., 377.

REDOX CONDITIONS DURING NEBULAR CONDENSATION. L. Grossman, Dept. of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, 5734 South Ellis Ave., Chicago, IL 60637. yosi@midway.uchicago.edu.

Theory: In thermodynamic calculations of molecular equilibria in high-temperature cosmic gases, $CO_{(g)}$ is so stable that it consumes the entirety of whichever of C or O is the lower in abundance, leaving the excess of the more abundant element to form other molecules and condensates. The best estimate of the solar C/O ratio is 0.50 [1,2], yielding oxide and silicate condensates, and of the H/O ratio is 2041 [3], yielding a very reduced system. Virtually all oxygen in excess of that in $CO_{(g)}$ and condensates reacts with hydrogen to form $H_2O_{(g)}$, and virtually all of the remaining hydrogen forms $H_{2(g)}$. During condensation of a solar gas at 10^{-3} b, the P_{H_2O}/P_{H_2} ratio falls gradually from $4.27\text{x}10^{-4}$ at 2000K to $3.95\text{x}10^{-4}$ at 1417K, then more steeply to $2.66\text{x}10^{-4}$ at 1300K, and levels off, reaching $2.52\text{x}10^{-4}$ at 900K [4], yielding log f_{O_2} from IW-6.8 (1500K) to IW-7.1.

Refractory Inclusions: Near-spherical white inclusions (CAIs), up to 1 cm in diameter, are found in CV3 chondrites at the ~5% level. Type As contain ~80% melilite and 20% spinel, with accessory clinopyroxene (cpx) and perovskite, while Type Bs contain ~40% melilite, 30% cpx, 20% spinel and 10% anorthite. Type B1s have a monomineralic melilite mantle, B2s do not. The mineralogy of CAIs indicates that their precursors are high-temperature solid condensates from the solar nebula [5], and their major element chemical and isotopic compositions indicate that they underwent later melting and partial evaporation [6]. The cpx, called "fassaite", contains 25% CaO, 10-22% Al_2O_3 and 1-20% TiO_2^{tot} (all Ti calculated as TiO_2). When $TiO_2^{tot} \geq 4$ wt%, chemical formulae calculated from EMP data on the basis of 6 oxygen anions and 1.00 Ca ion show Ti^{3+}/Ti^{tot} is 0.2 to 0.8, agreeing with optical [7] and XANES [8] spectral identification of Ti^{3+}. The assemblage spinel+melilite+fassaite, the latter of the same composition as that in CAIs, was crystallized from liquids having the compositions of CAIs under controlled f_{O_2} at 1500K [9], near the CAI solidus. From compositions of the synthetic phases and a non-ideal solution model for fassaite, equilibrium constants were determined for 2 reactions involving spinel, melilite and fassaite in which $O_{2(g)}$ converts Ti^{3+} into Ti^{4+}. From these and analyses of coexisting CAI phases, it was found that the log f_{O_2} at which the fassaite crystallized was -19.5±0.8 at 1500K, and that this applies to all 3 CAI types. This translates to IW-8.1±0.8, ≥0.5 log unit below that of a solar gas. Ti^{3+}-bearing fassaite is the only oxygen barometer that says that anything in chondrites formed in a gas that was near-solar in composition. This argues against CAI formation by repeated evaporation and condensation due to solar flares in a reconnection region close to the protosun, as one prediction of this is that CAIs would have formed from a very dust-enriched, and thus very oxidizing, gas [10]. Depletions of W and Mo relative to other refractory siderophiles in whole CAIs suggest they may contain trace components formed at higher f_{O_2} [11], and the presence in CAI rims of both pyroxene with low Ti^{3+}/Ti^{tot} [12] and Fe^{3+}-bearing andradite [5] implies that CAIs were affected by later events under much more oxidizing conditions. One idea is that such redox variability accompanied secondary exchange of ^{17}O and ^{18}O in disequilibrium reactions using atomic oxygen made by CO photolysis [13].

Fayalite in Chondritic Olivine: Solar gas is so reducing that metallic NiFe and pure forsterite co-condense at high T. FeO is eventually stabilized as fayalite, but only at such low T that slow Fe-Mg interdiffusion in olivine prevents 1 μ grains from reaching x_{Fa}=0.001, even for 10^6-yr nebular cooling times [4], far short of the apparent minimum x_{Fa} of the precursors of chondrules in UOCs, ~0.15. Models involving enhancement of O/H and O/C ratios by vaporization of regions enriched in dust relative to gas, formed by reasonable degrees of vertical settling [14] or radial transport [15] of dust, yield too low an f_{O_2} to overcome this major obstacle to understanding the oxidation state of chondrites.

References: [1] Allende Prieto C. et al. (2001) *Ap. J. Lett. 556*, L63-L66. [2] Allende Prieto et al. (2002) *Ap. J. Lett. 573*, L137-L140. [3] Anders E. & Grevesse N. (1989) *GCA 53*, 197-214. [4] Fedkin A. V. & Grossman L. (2005) *MESS II*. In press. [5] Grossman L. (1980) *Ann. Rev. Earth Planet. Sci. 8*, 559-608. [6] Grossman et al. (2000) *GCA 64*, 2879-2894. [7] Dowty E. & Clark J. R. (1973) *Am. Min. 58*, 230-242. [8] Simon S. B. et al. (2005) This volume. [9] Beckett J. R. (1986) PhD Thesis, Univ. Chicago. [10] Desch S. J. (2005) Pers. comm. [11] Fegley B. Jr. & Palme H. (1985) *EPSL 72*, 311-326. [12] Dyl K. A. et al. (2005) *LPSC XXXVI*, Abs. #1531(CD-ROM). [13] Clayton R. N. (2005) *LPSC XXXVI*, Abs. #1711(CD-ROM). [14] Cassen P. (2001) *Meteoritics Planet. Sci. 36*, 671-700. [15] Ciesla F. J. & Cuzzi J. N. (2005) Subm. to *Icarus*.

OXYGEN ISOTOPES OF INDIVIDUAL MINERALS IN THE PINK ANGEL. Yunbin Guan[1], Weibiao Hsu[2], Takayuki Ushikubo[1], Laurie A. Leshin[1,3], [1]Dept. of Geological Sciences, Arizona State University, Tempe, AZ 85287, USA. (yunbin.guan@asu.edu), [2]Laboratory for Astrochemistry and Planetary Sciences, Purple Mountain Observatory, Nanjing, 210008, China. (wbxu@pmo.ac.cn), [3]Center for Meteorite Studies, Arizona State University, Tempe, AZ 85287, USA. (laurie.leshin@asu.edu).

The Allende Pink Angel is a unique inclusion that was first described in [1]. It has a large pinkish interior (core) (90% of the total mass) surrounded completely by a whitish rim of ~400 μm wide. The interior is composed of a fine-grained, porous aggregate of Fe-rich spinel (60%), sodalite (30%), and grossular (5%). The rim is a compact assemblage of fine-grained spinel, anorthite, and diopside. We are carrying out correlated investigations of oxygen isotopes and of short-lived radionuclides in the Pink Angel. In this report, we present preliminary oxygen isotopic data for individual minerals in the Pink Angel.

In situ oxygen isotope analyses were carried out with the Cameca IMS 6f ion microprobe at Arizona State University. A total of 14 spots in one of the polished thin sections of the Pink Angel were measured and the results are plotted in Fig. 1. All the data plot along the carbonaceous chondrite anhydrous minerals (CCAM) line. Four spinel grains, one from the core and three from the rim, show "typical" ^{16}O-enrichments with δ^{18}O and δ^{17}O values at -44‰ to -50‰, similar to spinel from other Allende calcium-aluminum-rich inclusions (CAIs). Two diopside grains in the rim contain intermediate ^{16}O-excesses, plotting along the CCAM line at δ-values of -37‰ and -39‰.

One anorthite grain in the core has oxygen isotopes of about -15‰ for both δ^{18}O and δ^{17}O. However, two anorthite spots from the rim are less ^{16}O-enriched, with δ^{18}O = ~ -6‰ and δ^{17}O = ~ -9‰. Measurements of two sodalite grains, overlapping to small amounts of spinel and diopside, yielded oxygen isotopes of about -15‰, undistinguishable from the core anorthite. Sodalites of similar oxygen isotopic compositions with a larger variation range were also observed in a Ningqiang CAI [2]. The anorthite and sodalite in the Pink Angel are less depleted in ^{16}O than their counterparts in Allende CAIs [*e.g.*, 3]. The oxygen isotopic compositions of two grossular grains in the core are slightly heavier than those of sodalite and anorthite in the core, but similar to those of the two rim anorthites. One hedenburgite in the rim also plots on the CCAM line and is most ^{16}O-depleted among the phases measured, with δ^{18}O = 5‰ and δ^{17}O = -0.4‰.

The oxygen isotopes of sodalite, grossular, and even hedenburgite, which are believed to be alteration products of primary CAI minerals, all plot intriguingly along the CCAM line, probably produced by the same isotopic exchange between ^{16}O-rich solids and ^{16}O-poor nebular gas (or some other ^{16}O-poor components) as suggested for the isotopic heterogeneity among primary CAI minerals. Therefore, the alteration of the Pink Angel and the Ningqiang CAI [2] could have taken place in a nebular setting. Interestingly, sodalites from both inclusions contain ^{36}S excesses from *in situ* decay of the short-lived radionuclide ^{36}Cl [4, and unpublished data].

The Pink Angel thin sections used in this study are graciously provided by G. J. Wasserburg.

References: [1] Armstrong J. T. and Wasserburg G. J. (1981) *Proc. LPSC IX*, 1279-1303. [2] Guan Y. et al. (2005) *LPS XXXVI*, abstract # 2027. [3] Yurimoto H. et al. (1994) *EPSL 128*, 47-53. [4] Lin Y. et al. (2005) *PNAS 102*, 1306-1311.

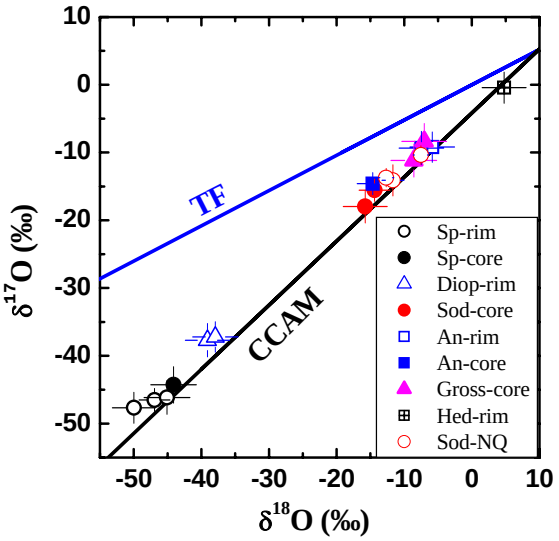


Fig. 1 Oxygen isotopes of individual minerals in the Pink Angel. Abbreviations: Sp – spinel; Diop – diopside; Sod – sodalite; An – anorthite; Gross – grossular; Hed – hedenburgite, TF – terrestrial fractionation line; CCAM – carbonaceous chondrite anhydrous minerals line; "core" and "rim" indicate that the minerals are from the core and rim of the Pink Angel, respectively. Sod-NQ represents data for sodalite in a Ningqiang CAI [2]. Error bars are 2σ.

OXYGEN ISOTOPE COMPOSITION OF SOLAR WIND IMPLANTED IN LUNAR SOILS: A ^{16}O-RICH PROTOSOLAR NEBULA. K. Hashizume[1] and M. Chaussidon[2], [1]Department of Earth & Space Sciences, Osaka University, Toyonaka, Osaka 560-0043, Japan (kohash@ess.sci.osaka-u.ac.jp), [2]CRPG-CNRS, BP 20, 54501 Vandoeuvre-lès-Nancy Cedex, France (chocho@crpg.cnrs-nancy.fr).

The discovery of strong ^{16}O enrichments in Ca-Al-rich inclusions from carbonaceous chondrites [1] was followed in the last 30 years by a systematic search for non mass-dependant oxygen isotopic anomalies in all available solar system rocks [*e.g.*, 2]. The picture which emerged from these studies is that most of the chondritic and achondritic meteorites as well as Earth and Mars have variable bulk oxygen isotopic compositions which cannot be derived one from others by 'normal' chemical and physical processes obeying mass dependent fractionation laws. The mass dependence of rate constants and equilibrium constants of most chemical/physical processes dictates that the abundance ratios of the three stable oxygen isotopes in all solar system objects should be related by a law which can be described by the approximated equation $\delta^{17}O = 0.52 \times \delta^{18}O$ (the terrestrial fractionation line). The fact that the oxygen isotopic composition of most meteorites are distributed on both sides of this line has been interpreted as reflecting either (i) the presence in the solar accretion disk of grains and gas which differed in their relative ^{16}O contents because of different nucleosynthetic origins and which were mixed in various proportions [1,2] or (ii) the occurrence in the early solar system of peculiar reactions in the gas phase which would not obey the mass fractionation laws [3-5].

Central to this issue is the O isotopic composition of the protosolar gas from which all early solar system solids derive. This composition is not known but is likely preserved in the outer layers of the Sun. Using the successful technique we have previously applied for identification of the solar composition of N [6] and C [7] from lunar samples, we have attempted to determine the O isotopic composition of the Sun [8].

We have analyzed so far ~40 metallic grains collected from the Apollo 17 soil sample 79035. Most of the metallic grains were enveloped with oxide layers whose thicknesses were 100-500 nm. The O concentrations of this layer were as high as ~30 wt%, which are enough to totally mask the solar wind component whose concentration is expected to be ~1 wt% at most, as derived from our previous estimate of solar wind C concentration among grains from the same sample [7]. The $\Delta^{17}O$ values ($\equiv \delta^{17}O - 0.52 \times \delta^{18}O$) of the oxide layers for most of the grains were ~0 ‰, suggesting a terrestrial origin of these oxides [8]. However, a small fraction of metallic grains (~10%) exhibited a surface correlated O component with a significantly positive $\Delta^{17}O$ value, up to $+8.3 \pm 2.2$ ‰ (1σ). Detection of such ^{16}O depleted component among lunar grains is compatible with the result of Ireland *et al.* [9] who observed among metallic grains from lunar soil 10084, an O component with a $\Delta^{17}O$ value of about +27 ‰, although $\delta^{18}O$ values are largely different: our samples showed negative values (-10 ‰ or lower), whereas their grains showed positive values up to +100 ‰. The high O concentration of our observed ^{16}O depleted component, up to 24 wt%, suggests a non-solar origin of this component. Although it is still premature to identify the nature of this component from the current data sets, we suspect contribution of planetary components with positive $\Delta^{17}O$ values [*e.g.*, 10] supplied to the Moon surface.

At depth in the grains (>500 nm), below the above mentioned oxide layers, we observed a tenuous (<1 wt%) but clearly visible component which is strongly enriched in ^{16}O. This component is attributable to the implanted solar energetic particles [8]. We conclude that the solar gas, compared to the terrestrial composition, is enriched in ^{16}O, by at least 20 ‰ in $\Delta^{17}O$. Our conclusion suggests that O in Earth, Mars, Moon and meteorites, which is in bulk depleted in ^{16}O, must have originated from precursors which were produced by 'specific reaction pathways', as recently proposed [*e.g.* 3-5,11-13], and was thus strongly isotopically fractionated in a non-mass dependant way from the protosolar nebular gas.

[1] Clayton R. N., *et al.* (1973) *Science* **182**, 485-488. [2] Clayton R. N. (1993) *Annu. Rev. Earth Planet. Sci.* **21**, 115-149. [3] Thiemens M. H. & Heidenreich J. E. (1983) *Science* **219**, 1073-1075. [4] Marcus R. A. (2004) *J. Chem. Phys.* **121**, 8201-8211. [5] Clayton R. N. (2002) *Nature* **415**, 860-861. [6] Hashizume K., *et al.* (2000) *Science* **290**, 1142-1145. [7] Hashizume K., *et al.* (2004) *Astrophys. J.* **600**, 480-484. [8] Hashizume K. & Chaussidon M. (2005) *Nature* **434**, 619-622. [9] Ireland T. R., *et al.* (2005) *LPS* **XXXVI**, Abstract#1572. [10] Choi B.-G. *et al.* (1998) *Nature* **392**, 577-579. [11] Yurimoto H. & Kuramoto K. (2004) *Science* **305**, 1763-1766. [12] Lyons J. R. & Young E. D. (2005) *Nature* **435**, 317-320. [13] Chakraborty S. & Thiemens M. H. (2005) *LPS* **XXXVI**, Abstract#1113.

OXYGEN-16 VARIATIONS IN THE SOLAR SYSTEM: THE POSITIVES AND NEGATIVES. T. R. Ireland, Research School of Earth Sciences, The Australian National University, Canberra ACT 0200, Australia <Trevor.Ireland@anu.edu.au>.

Introduction: The ^{16}O isotopic variations in oxygen from refractory materials have colored meteoritics research for over 30 years [1]. While isotopic anomalies in titanium and magnesium can be ascribed to nucleosynthetic processes (producing enhanced ^{50}Ti and ^{26}Al), the systematics of oxygen isotopic variations have not been so easy to delineate. While initially portrayed as a nucleosynthetic component, the lack of correlation with other isotopic anomalies, makes this an unsatisfactory explanation [e.g. 2]. The discovery of chemically-induced mass independent isotope fractionation and similar variations in Earth's atmosphere [3] opened a new way of looking at the anomalies, but the specific mechanism that might operate in the early solar system has been lacking. Most recently, production of ^{16}O variations through predissociation mechanisms, both in the molecular cloud and in the solar nebula, have attracted attention [4-6].

^{16}O-enrichments and depletions: A prediction of any of the chemical isotope fractionation models is the production of complementary ^{16}O-enriched and ^{16}O-depleted components. In Earth's atmosphere, oxygen becomes isotopically lighter, while ozone is heavy. In the UV photochemistry models, predissociation of CO leads to isotopically light CO, and isotopically heavy O radicals that react with protons to form water ice, or react with solids surfaces to produce local oxidation. For example, it is predicted that cometary water ice should be isotopically very heavy [4] and variations in dust/gas ratios in the early solar system may produce reservoirs with heavy oxygen [7].

^{16}O depletions in lunar metals: Oxygen with a 5% depletion in ^{16}O exists in lunar metals grains [8]. This oxygen signal is preserved approximately 2nm below the surface in metals grains from lunar soil 10084. After removal of isotopically normal surface oxidation (either lunar or terrestrial), the oxygen concentration decreases, but the composition in terms of ^{16}O excess remains constant until the signal has decayed after a few hundred nanometers. The depth control is provided by the sputter rate of Cs^+ ions into Fe-rich matrices (metals and oxides), but the depth calibration for the metal grains is complicated because the grain geometry is altered when the grains are pressed in to gold. The preservation of an anomalous oxygen component below the surface and the constancy of the composition with depth (notwithstanding possible changes in mass-dependent fractionation) suggest solar wind implantation.

Hashizume and Chaussidon [9] have also measured lunar metal grains and find extensive surface oxidation with isotopically normal oxygen persisting to depths of over 1000 nm. In a few cases, the apparent ^{16}O excess rises with depth, that is, there appears to be an un-mixing of the surface isotopically normal oxygen and a component preserved at depth that is enriched in ^{16}O, and attributable to ^{16}O-rich solar energetic particles. Hashizume and Chaussidon [9] therefore conclude that the solar composition is, at a minimum, enriched in ^{16}O by 4%.

These two data sets, from [8] and [9] respectively, are therefore at odds with each other and require explanation. The difference in the data is very marked. The grains analyzed by Ireland et al. [8] had very shallow effects of surface oxidation (order 10 wt% of oxygen to a few nm) while the metal grains analyzed by Hashizume and Chaussidon show persistent surface oxidation (oxygen concentration of over 10 wt % persisting to near 200 nm). The anomalous composition measured by [8] was constant with depth, the anomalous composition measured by [9] was seen in only 5 grains of 134 and persistently changed with depth. These are clearly different samples from the Moon reflecting dramatically different histories. But, they are both from the Moon, and the differences between the data sets offer the prospect of resolving some long-standing issues concerning the preservation of solar wind on the Moon.

The key questions for resolving the issues between the lunar metal data sets are: 1) how widespread is the ^{16}O depleted composition in lunar soils? 2) Is surface oxidation produced on the Moon and under what conditions? 3) Is the Sun isotopically heavy by 5 % or is another source possible?

References: [1] Clayton R. N et al. (1973) *Science,* **182**, 485. [2] Ireland T. R. and Fegley B. Jr (2001) *Int Geol. Review*. **42**, 865. [3] Thiemens M. (1999) *Science,* **283**, 341. [4] Yurimoto H. and Kuramoto K. (2004) *Science,* **305**,1763. [5] Clayton R. N. (2002) *Nature,* **415**, 860. [6] Lyons, J. and Young E. D. (2005) *Nature,* **435**, 317. [7] Wiens, R.C., et al. (1999), Meteoritics & Planetary Science, **34**, 99. [8] Ireland T. R. et al. (2004) *Lunar Planet. Sci*. **XXXV**, Abstract #1572. [9] Hashizume K. and Chaussidon M. (2005) *Nature,* **434**, 619.

DENSITIES OF THE SATURNIAN SATELLITES AND THE C/O CHEMISTRY OF THE SOLAR NEBULA

T. V. Johnson (Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA), J. I. Lunine (Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, USA)

The composition of material condensed from a solar composition nebula is highly dependent on the abundance of oxygen, the dominant solid forming element (silicates and water ice), and carbon, roughly half as abundant. These abundances, and the partition of gaseous C between CO and CH_4, determine the relative abundances of water ice and rock/metal in the solid condensates. The mean densities of satellites made from this material reflect the rock, metal and ice abundances, corrected for the effects of pressure and porosity. Recently proposed changes to the solar abundance values for carbon and oxygen have a large effect on the expected density solar composition condensates. The effects of these changes on the interpretation of new satellite density determinations from the Cassini mission include: 1. Solar composition condensates have higher mean densities regardless of the state of gas phase carbon, 2. Phoebe is significantly denser, for plausible porosities, than the regular icy satellites and is likely representative of solar nebular condensates in CO-rich conditions in the outer solar system rather than circum-Saturn planetesimals, 3. The mass-weighed average icy satellite density (~1220 kg m^{-3}) is too low for a solar composition condensate from either the solar nebula or a circumplanetary nebula unless significant amounts of carbon were incorporated as low density solids, and 4. Large variations in mean density among the icy satellites imply post-formation fractionation processes that result in significant differences in current ice to rock/metal proportions. A portion of this work was done at the Jet Propulsion Laboratory, Caltech, under a grant from NASA.

TRANSITION ELEMENT (Fe, Cr, AND Mn) OXIDATION STATES RECORDED IN PRIMITIVE INTERPLANETARY DUST. Lindsay P. Keller[1] and Akiko Takayama[2], [1]ARES, Mail Code KR, NASA Johnson Space Center, Houston, TX 77058, [2]Faculty of Science, 1-1, Rokkodai, Nada-ku, Kobe JAPAN 657-8501 (Lindsay.P.Keller@jsc.nasa.gov).

Introduction: Anhydrous interplanetary dust particles (IDPs) contain abundant presolar materials including silicate stardust [1] and preserved molecular cloud organic matter [2, 3]. Other primitive characteristics include high porosity, higher abundances of carbon, nitrogen, and volatile trace elements than CI chondrites, and an anhydrous mineralogy dominated by Mg-rich crystalline silicates such as enstatite and forsterite along with abundant amorphous silicates. Some of these anhydrous IDPs are linked directly to cometary sources based on estimates of their atmospheric entry velocities [4]. The anhydrous IDPs are likely representative samples of the building blocks of the solar system – a complex mixture of nebular and presolar materials largely unperturbed by secondary processing.

Results and Discussion: Enstatite and forsterite grains in IDPs typically contain minor Cr and Mn contents (up to 5 wt.% as oxides) and in many cases their abundance exceeds that of Fe (Fig. 1). Low-Fe, Mn-rich forsterites were identified in IDPs by Klöck *et al.* [5] and have also been observed in some primitive meteorites [5, 6]. The Mn-rich forsterite and enstatite are believed to have formed via gas-solid condensation in the nebula [5, 6], with forsterite forming at higher temperatures than enstatite. It is not known whether the Cr in these silicates is di- or trivalent, but Na is not detected in the pyroxenes, so the charge balanced substitution $NaCr^{3+}$ for 2Mg does not appear to be operating – this suggests Cr^{2+} substitution for Mg, in both pyroxene and olivine. Minor diopside grains in anhydrous IDPs tend to be more Cr-rich than enstatite in the same particles.

Amorphous silicates (GEMS, glass with embedded metal and sulfides) are abundant in these primitive IDPs and also record variable oxidation states. We proposed that most GEMS grains are non-equilibrium condensates that formed after high temperature crystalline silicates (forsterite, enstatite, diopside) condensed, but prior to the main phase of sulfide formation/condensation [7]. In this scenario, conditions during condensation were sufficiently reducing to keep Fe in the metallic state to at least temperatures below ~1000K (the upper stability limit for the preservation of the amorphous silicate matrix before it anneals [8]) and Fe^{2+} only became abundant when sulfidization reactions began at ~700K. Individual GEMS grains can contain both nanophase kamacite and taenite, however, their compositions are not in equilibrium [9]. In our X-ray mapping experiments, we have also identified Fe- and Cr-rich grains within GEMS – detailed transmission electron microscope measurements are underway to determine if these are nanophase metal or chromite grains [9]. Our mapping experiments also show that the amorphous silicate matrix of GEMS grains tends to be highly SiO_2 normative with much of the Fe present as metal. However, we have measured Fe oxidation states in some FeS-free GEMS grains and have documented a mixture of Fe metal and Fe^{2+} in the amorphous silicate matrix [7].

Sulfides in IDPs are predominantly pyrrhotite and occur as large single crystal grains and as nanophase grains attached to the surfaces of GEMS grains. Rare grains of Zn-rich sulfide occur in these IDPs and suggests that Zn behaves as a chalcophile element.

References: [1] Messenger, S. *et al.* (2003) *Science*, **300**, 105. [2] Messenger, S. (2000) *Nature*, **404**, 968. [3] Keller, L. P. *et al.* (2004) *GCA*, **68**, 2577. [4] Brownlee, D. E. *et al.* (1995) *LPSC*, **26**, 183. [5] Klöck, W. *et al.* (1989) *Nature*, **339**, 126. [6] Weisberg, M. K. *et al.* (2004) *MAPS*, **39**, 1741. [7] Keller, L. P. & Messenger, S. (2004) *LPSC* **35**, 1985. [8] Brownlee, D. E. *et al.* (2005) *LPSC* **36**, 2391. [9] Keller, L. P. *et al.* (2005) *LPSC* **36**, 2088.

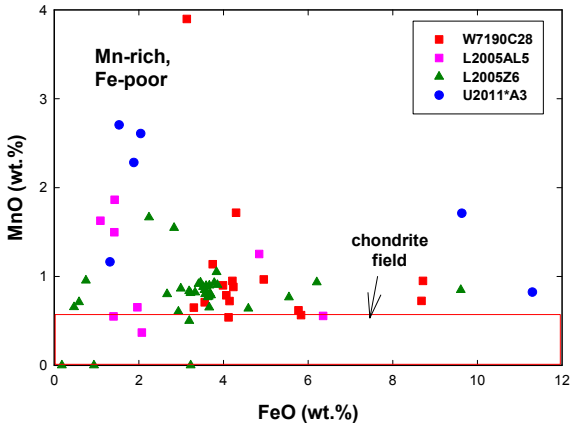


Figure 1. Compostions of pyroxene grains in anhydrous IDPs with unusual Mn-rich compositions – also plotted is the field for meteoritic pyroxene compositions from [5].

OXYGEN ISOTOPIC COMPOSITIONS OF CHONDRULES. A. N. Krot[1], R. H. Jones[2], M. Yoshitake[3], and H. Yurimoto[4], [1]University of Hawai'i at Manoa, USA (sasha@higp.hawaii.edu). [2]University of New Mexico, USA. [3]Kobe University, Japan. [4]Hokkaido University, Japan.

It is generally believed that chondrules formed by varying degrees of melting of dense aggregates of Fe-Mg silicate, metal, and sulfide grains during repetitive flash-heating events in the dusty solar nebula. O-isotopic compositions of chondrules may have recorded various stages of chondrule evolution: the assemblage of isotopically heterogeneous precursor grains, O-isotopic exchange with the surrounding gas during chondrule melting, and O-isotopic exchange during postcrystallization alteration. Conventional bulk and *in situ* ion microprobe measurements of O-isotopic compositions of chondrules and chondrule minerals [1-19], in combination with O-isotopic diffusion and exchange experiments on chondrule-like melts and minerals [20-22] and theoretical modeling [23-28] provide important constraints on the evolution of O-isotopic compositions of the inner solar nebula, the nature of chondrule-forming processes, and the genetic relationship between refractory inclusions and chondrules, and are reviewed here.

Bulk O-isotopic compositions of chondrules show large diversity both among and within the various chondrite groups [29-34]. On a three-oxygen diagram, bulk O-isotopic compositions of most chondrules in ordinary (O), enstatite (E), and carbonaceous (C) chondrites plot above, along, and below terrestrial fractionation line, respectively. These observations are commonly interpreted as a result of stochastic sampling of isotopically heterogeneous precursor materials and O-isotopic exchange with a common gaseous reservoir with $\Delta^{17}O$ of +2‰ to +8‰ [29,35]. In addition, bulk O-isotopic compositions of chondrules were probably modified to various degrees during postcrystallization alteration, most likely in an asteroidal setting [e.g., 36].

Ion microprobe measurements of O-isotopic compositions of chondrules have been reported for O, E, and C chondrites [1-19]. Most analyses of Fe-Mg chondrules are limited to olivine grains; measurements of multiple mineral phases within a single chondrule are exceptionally rare [3,10,25]. Al-rich chondrules with relict CAIs have been studied in greater details [4,6,9,10,13,14,16,25].

Most chondrules are ^{16}O-depleted ($\Delta^{17}O \geq$ -7‰) relative to AOAs and most CAIs ($\Delta^{17}O \leq$ -20‰), suggesting formation in isotopically distinct reservoirs [24,27,28]. The only exceptions are chondrules and CAIs in the metal-rich CH and CB chondrites. In the CB chondrites Hammadah al Hamra 237 and QUE94411, the CAIs appear to have been melted; they are uniformly ^{16}O-depleted ($\Delta^{17}O$ = -10‰ to -6‰) and overlap in composition with chondrules ($\Delta^{17}O$ = -7‰ to -1‰) [7]. This anomaly may be due to a planetary formation mechanism of the CB chondrites [37]. Some CAIs in CH chondrites are uniformly ^{16}O-depleted to a level observed in most CH chondrules [18,38,39]. The uniformly ^{16}O-rich chondrules ($\Delta^{17}O \leq$ -20‰) are exceptionally rare and have been found only in CH chondrites [5,18].

Most Fe-Mg chondrules from primitive chondrites are isotopically uniform (within 2-3‰ in $\Delta^{17}O$); O-isotopic heterogeneity is due to the presence of relict grains which appear to represent either chondrules of earlier generations or incompletely melted refractory inclusions [3,10,11,19,25]. The Al-rich chondrules with relict CAIs have heterogeneous O-isotopic compositions ($\Delta^{17}O$ from -20‰ to 0‰), with the relict grains being ^{16}O-enriched compared to the chondrule phenocrysts and mesostasis. The Al-rich chondrules without relict CAIs are isotopically uniform and have ^{16}O-poor compositions similar to those of Fe-Mg chondrules.

We infer that O-isotope compositions of chondrules from primitive chondrites resulted from two mayor processes: homogenization of isotopically heterogeneous materials during chondrule melting, and O-isotopic exchange between chondrule melt and ^{16}O-poor nebular gas. In contrast to most refractory inclusions, chondrules appear to have largely originated from ^{16}O-poor precursors and were subsequently melted in the presence of ^{16}O-poor nebular gas. If the initial composition of the solar nebula was ^{16}O-rich [40], chondrule precursors must have been thermally processed in an ^{16}O-poor gas. Because chondrules without relict grains in CR carbonaceous chondrites are isotopically uniform [10] and distinct from those in O chondrites, O-isotopic exchange with a common gaseous reservoir seems unlikely.

These observations can be interpreted in terms of isotopic self-shielding during UV photolysis of CO in the initially ^{16}O-rich ($\Delta^{17}O$ ~ -25‰) protoplanetary disk or parent molecular cloud [25,26,28,40]. According to these models, the UV photolysis preferentially dissociates $C^{17}O$ and $C^{18}O$ in the peripheral zones of the protoplanetary disk or the parent molecular cloud. If this process occurs in the stability field of water ice, the released atomic ^{17}O and ^{18}O are incorporated into water ice, while the residual CO gas becomes enriched in ^{16}O. The inner solar nebula had initially solar H_2O/CO ratio and was ^{16}O-rich. During this time, the ^{16}O-rich CAIs and AOAs, and some chondrules formed. Subsequently, the inner solar nebula became H_2O-enriched and ^{16}O-depleted, because meter-size icy bodies, which were enriched in $^{17,18}O$, agglomerated outside the snowline (~5 AU), drifted rapidly towards the Sun and evaporated. During this time, which may have lasted for ~ 3 Myr, most of the chondrules and ^{16}O-depleted igneous CAIs formed [25].

References: [1] Ash et al. (2000) *MAPS, 35,* A21. [2] Guan et al. (2004) *LPS, 35,* 9083. [3] Jones et al. (2004) *GCA, 68,* 3423. [4] Kimura et al. (2004) in CPD, 9029. [5] Kobayashi et al. (2003) *Geochem. J., 37,* 663. [6] Krot et al. (1999) *MAPS, 34,* A68. [7] Krot et al. (2001) *MAPS, 36,* 1389. [8] Krot et al. (2004) *LPS, 35,* 1389. [9] Krot et al. (2004) *MAPS, 39,* A56. [10] Krot et al. (2005) *GCA,* submit. [11] Kunihiro et al. (2004) *GCA, 68,* 3599. [12] Leshin et al. (1998) *MAPS, 33,* A93. [13] Maruyama & Yurimoto (2003) *GCA, 67,* 3943. [14] Maruyama et al. (1999) *EPSL, 169,* 165. [15] Nakamura et al. (2002) *SAM, 27,* 115. [16] Russell et al. (2000) *EPSL, 184,* 57. [17] Varley et al. (2002) *MAPS, 37,* A143. [18] Yoshitake & Yurimoto (2004) in CPD, 9062. [19] Yurimoto & Wasson (2002) *GCA, 66,* 4355. [20] Boesenberg et al. (2004) in CPD, 9047. [21] Ryerson & McKeegan (1994) *GCA, 58,* 3713. [22] Yu et al. (1995) *GCA, 59,* 2095. [23] Clayton (2002) *Nature, 415,* 860. [24] Krot et al. (2002) *Science, 295,* 1051. [25] Krot et al. (2005) *ApJ, 622,* 1333. [26] Lyons & Young (2005) *Nature, 435,* 1317. [27] Scott & Krot (2001) *MAPS, 36,* 1307. [28] Yurimoto & Kuramoto (2004) *Science, 305,* 1763. [29] Clayton et al. (1983) in Chondrules and Their Origins, ed. E. A. King, Houston: LPI, 37. [30] Clayton & Mayeda (1985) *LPS, 16,* 142. [31] Clayton et al. (1991) *GCA, 55,* 2317. [32] Clayton (1993) *Ann. Rev. Earth Planet. Sci., 21,* 142. [33] Rubin et al. (1990) *EPSL,* 96, 247. [34] Wasson et al. (2000) *GCA, 64,* 1279. [35] Jones et al. (2004) *LPS, 35,* 1865. [36] Young et al. (2002) *GCA, 66,* 683. [37] Krot et al. (2005) *Nature,* in press. [38] Makide et al. (2004) in CPD, 9076. [39] Sahijpal et al. (1999) *MAPS, 34,* A101. [40] Hashizume & Chaussidon (2005) *Nature, 434,* 619.

OXYGEN ISOTOPES OF MATRIX OF PRIMITIVE METEORITES AND IMPLICATIONS TO NEBULAR DUST. T. Kunihiro[1], K. Nagashima[2], A. Brearley[3], and H. Yurimoto[4], [1]University of California, Los Angeles, CA 90095 (tky@ess.ucla.edu), [2]University of Hawaii at Manoa, Honolulu, HI 96822, [3]University of New Mexico, Albuquerque NM 87131, [4]Hokkaido University, Sapporo 0600810 Japan.

Introduction: Since the sun contains >99% of the mass of the solar system, its composition is considered representative of the solar nebula. The similar abundances of the carbonaceous chondrite nonvolatile elements to those of the solar photosphere are a major reason why the carbonaceous chondrites are of such great interest in modeling of the formation and early evolution of planetary materials in the solar nebula. The carbonaceous chondrites are comprised of three major components: refractory inclusions, chondrules, and fine-grained matrix. As a major component of carbonaceous chondrites, the matrix plays an important role in the search for pristine fine-grained nebular material in the solar nebula.

After oxygen isotopic anomalies were observed in refractory inclusions [1] many O-isotope studies have been made on refractory inclusions and chondrules; however, the fine-grained nature of the matrix was a limiting factor in determining O-isotope compositions of the specific constituents of the matrix.

Mineralogy and bulk O-isotope compositions of matrices: Matrix materials are diverse in character and vary from one chondrite group to another; however, in general, the matrix is largely composed of a complex assemblage of highly unequilibrated material consisting of silicates (dominantly FeO-rich olivine), oxides, sulfides, sulfates, carbonates, Fe-Ni metal, phyllosilicates, and amorphous and carbonaceous materials [2]. Matrix of highly pristine chondrites, such as Acfer 094, lacks phyllosilicates and consists largely of small crystalline silicates that are embedded in amorphous material [3]. The grain sizes of its constituent minerals range from ~5 μm down to 10 nm. Although the disequilibrium nature of the matrix would lead one to expect heterogeneous O-isotope distribution among minerals, the bulk O-isotope compositions of the matrix in several carbonaceous chondrites plot as a cluster on the CCAM line or slightly below, with $\delta^{18}O$ varying from 0 to 15‰ [4]. The distinct differences in the bulk O-isotope composition between matrices and chondrules (or refractory inclusions) imply that they were not derived directly from one another.

Micro-distribution of O-isotope compositions: Recently an in-situ and high-precision isotopic imaging technique (isotopography) has been developed [5] and applied to the matrix of Vigarano [6-7] and Acfer 094 [8]. The O-isotopes are distributed heterogeneously in the matrix on a micrometer-scale. They plot along the CCAM line with $\delta^{18}O$ varying from ~-50 to ~10‰, consistent with O-isotope variations observed in chondritic components. Some 2 μm grains are ^{16}O-rich and others are ^{16}O-poor, and they are dispersed throughout the matrix. The O-isotopes in most of the matrix are ^{16}O-poor and are distributed homogeneously. Submicron presolar-silicates with distinct O-isotope compositions are also embedded in the matrix of Vigarano and Acfer 094 although the abundances are extremely low (<30 ppm [7-8]). The degree of aqueous alteration is more extensive in Vigarano than in Acfer 094 [3, 9]. The existence of preserved submicron presolar-silicates in both Vigarano and Acfer 094 matrices with similar O-isotope distribution suggests that O-isotopes in the matrices are not completely modified by aqueous alteration and that the matrices retain O-isotope distributions of the nebular dust.

Implications to nebular dust: O-isotopes show that the matrix is a mechanical aggregate of fine-grained materials mainly formed in the solar system; small amounts of presolar grains also are dispersed in the matrix. More than 95% of matrix grains are depleted in ^{16}O and equivalent to the bulk matrix. The rest are mainly ^{16}O-enriched grains related to refractory inclusions. The low abundance of presolar grains indicates that most of presolar grains cannot survive in the solar nebular, i.e., they had been destroyed during nebular processes. O-isotopic equilibration with nebular gas is a probable explanation for the predominance of ^{16}O-depleted materials in the matrices. If so, the gas-solid equilibration was almost completed before chondrite parent-body accretion in the solar nebula.

References: [1] Clayton et al. (1973) *Science*, **182**, 485 [2] Brearley (1996) In *Chondrules and the Protoplanetary Disk*, 137 [3] Greshake (1997) *GCA* **61**, 437 [4] Clayton and Mayeda (1999) *GCA*, **63**, 2089 [5] Yurimoto et al. (2003) *Appl. Sur. Sci.* [6] Kunihiro et al. (2005) *GCA*, **69**, 763 [7] Nagashima et al., in preparation [8] Nagashima et al. (2004) *Nature*, **428**, 921 [9] Lee et al. (1996) *MAPS* **31**, 477

OXYGEN ISOTOPIC EVOLUTION DURING THE FORMATION AND EVOLUTION OF THE SOLAR NEBULA: MOLECULAR CLOUD ORIGIN HYPOTHESIS FOR THE ISOTOPIC ANOMALY AND ITS IMPLICATIONS. Kiyoshi Kuramoto and Hisayoshi Yurimoto, *Hokkaido University, Sapporo 060-0810, Japan, (keikei@ep.sci.hokudai.ac.jp).*

Observations and theory strongly suggest that significant mass-independent isotopic fractionation occurs between CO and H_2O molecules within a molecular cloud core from which a proto-planetary system forms. Such isotopic anomalies may be transported to proto-planetary disk and trapped into heterogeneously into rocky components in the inner disk. This model provides a plausible explanation for the origin of heterogeneous oxygen isotope compositions among meteorites and their inclusions, and also some predictions which would become testable in future.

Molecular cloud chemistry: Since stars form in clustered environment, star-forming molecular cloud is irradiated by the energetic photons emitted from young stellar objects and possibly from massive stars if they coexist. Observational data [1,2] and numerical models [3] reveal selective ultra-violet dissociation of $C^{17,18}O$ isotopomers by the self-shielding effect of $C^{16}O$, the dominant O-bearing gas species in molecular clouds. Since released atomic oxygen is likely adsorbed and then hydrogenated to H_2O on dust grains, H_2O ice produced in molecular cloud is expected to be ^{16}O-depleted. A mass balance consideration predicts that H_2O ice and CO have ^{16}O-poor ($\delta^{17,18}O_{MC} = 100 \sim 250‰$) and ^{16}O-rich ($-60 \sim -400‰$, which is consistent with observational constraint) compositions relative to the bulk molecular cloud, respectively [4]. This naturally explains the ^{16}O-depleted nature of H_2O in the early solar nebula inferred from meteoritic minerals altered by H_2O [5].

Dust-gas fractionation in an accreting proto-planetary disk: A dust grain immersed in a proto-planetary disk has relative motion against ambient disk gas which rotates with speed slightly lower than the Keplerian owing to the support of radial pressure gradient. The frictional loss of angular momentum due to their relative motion causes the drift of grain toward the central star. Considering the gradual growth of dust grains from interstellar sub μm size by coagulation as well as the decay of gas accretion, a proto-planetary disk should have experienced a stage during which solid grains preferentially infall toward the central star. During this stage, solid grains release H_2O vapor to disk gas after the passage of the snow line and thereby enhance the H_2O vapor content in the inner disk. A two-fluid disk model predicts that enrichment with factor of several is possibly achieved in an inner disk when the disk accretion rate decreases to 10^{-8} $M_\odot$/yr (typical for classical T-tauri star) or below and the dust grains grow to mm-size [6]. This means that the inner solar nebula may become ^{16}O-poor by several tens permils in average during such stage because H_2O is predicted to be significantly ^{16}O-poor. Such moderate H_2O enhancement is sufficient to explain the relative depletion in ^{16}O (difference in $\delta^{17,18}O \approx +50‰$) seen for the major part of the meteoritic materials relative to typical ^{16}O-rich CAIs, assuming that the latter have formed before the development of H_2O enrichment [4]. This is consistent with the maintenance of CAI and chondrule reprocessing after the main phase of ^{16}O-rich CAI formation [7,8]. Above interpretation predicts that the Sun is ^{16}O-rich, which is consistent with the ^{16}O-rich composition of implanted solar wind extracted from lunar soil [9].

Relationship with diversity in redox state of primitive meteorites: The preferential infall of dust grains is also expected to cause a heterogeneous enrichment of reduced C-bearing vapors in the innermost disk through the vaporization of organic matters contained in dust grains. In particular, the change in disk accretion rate possibly causes large variation of C/O ratio as well as H_2O content within the inner disk. Before the H_2O-enriched nebular gas is transported to the disk center, the innermost disk possibly has high C/O ratio allowing the formation of SiC, which might play an important role in the Si/Mg fractionation as well in the control of redox state inferred from the chemical systematics of chondrites [6,10].

Outer planets as diagnostics to test models: Our model predicts that the outer planets have ^{16}O-depleted compositions because they are enriched in heavy elements originally coexisted with H_2O ice as nebular dust components. The depletion increases with increasing heavy element enrichment. On the basis of chemical composition of their atmospheres, Jupiter, Saturn and Uranus/Neptune are estimated to have bulk isotopic compositions more than +35, 50, and 65‰ difference in $\delta^{17,18}$O relative to the Sun, respectively [6]. The outer planets and their satellites may provide key diagnostics to test the models which attempt to explain the O-isotopic heterogeneity in the meteorites and rocky planets. This is because alternative models predict different O-isotopic composition for the outer planets. For instance, the model assuming the CO self-shielding at the inner edge of the solar nebula [11] implies little depletion in ^{16}O relative to the Sun and that assuming the CO self-shielding at the surface skin layer of the solar nebula [12] implies poor correlation between the isotopic composition and heavy element enrichment.

References:

[1] Lada, C. J., Lada, E. A., Clemens, D., & Bally J.(1994) *Astrophys. J.*, **429**, 694. [2] Ando, M. et al.(2002), *Astrophys. J.*, **574**, 187. [3] Warin, S., Benayoun, J. J., & Viala, Y. (1996) *Astron. Astrophys.*, **308**, 535. [4] Yurimoto, H. & Kuramoto, K. (2004) *Science*, **305**, 1763. [5] Choi, B., McKeegan, K. D., Krot, A. N., & Wasson, J. T. (1998) *Nature*, **392**, 577. [6] Kuramoto, K. & Yurimoto, H. (2005) in *Chondrites and the Protoplanetary Disk*, eds A. N. Krot, E. R. D. Scott, and B. Reipurth, 181. [7] Amelin, Y., Krot, A. N., Hutcheon, I. D., & Ulyanov, A. A. (2002) *Science*, **297**, 1680 [8] Krot, A.N., Yurimoto, H., Hutcheon, I. D., & MacPherson, G. J. (2005) *Nature*, **434**, 998 [9] Hashizume, K., & Chaussidon, M. (2005) *Nature*, **434**, 619. [10] Fukui, T. and Kuramoto, K. (2005) this issue. [11] Clayton, R. N. (2002), *Nature*, **415**, 860. [12] Lyons, J. R., & Young, E. D. (2005), *Nature*, **435**, 317.

CO SELF-SHIELDING IN THE SOLAR NEBULA J. R. Lyons[1], [1]Institute of Geophysics and Planetary Physics, and Department of Earth and Space Sciences, UCLA, Los Angeles, CA 90095; jrl@ess.ucla.edu

Introduction: Clayton's suggestion [1] that CO self-shielding in the X-point region of the nebula was the source of a ^{16}O-depleted H_2O reservoir, as required by the two-component mixing model for CAIs [2], has led to recent work on the topics of self-shielding [3,4] and the oxygen isotope composition of the solar wind [5]. Here I will present a review of CO self-shielding in the solar nebula.

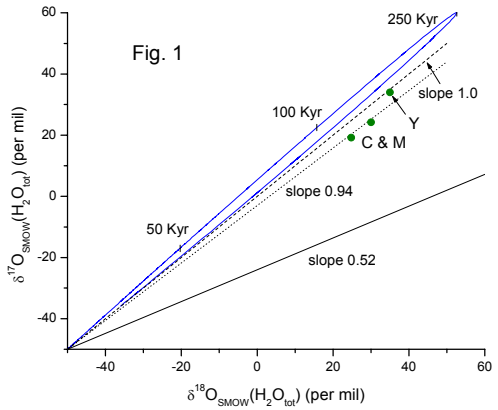
CO self-shielding in the inner solar nebula: Self-shielding of CO in the inner solar nebula is advantageous for two reasons: 1) a very high flux of far ultraviolet (FUV) photons was available from the protosun, and 2) the transport timescales to go from ~ 0.1 AU to ~ 2 AU are fairly short, especially if particles were carried by the X-wind. The disadvantages of CO self-shielding in the inner solar nebula are several [6]: 1) high temperatures reduce the effectiveness of self-shielding [7], 2) strong continuum absorption due to gas-phase H_2O, and 3) high temperature reactions of C with H_2 and H_2O eventually reforms CO, erasing the anomalous isotope signature produced by CO self-shielding.

At 2000 K and 10 mbar, the following reaction sequence will occur (the chemical loss timescale for leftmost reactant is shown) [6]:

$$CO + h\nu \rightarrow C + O \qquad \sim 10^{2}\ \text{sec}$$
$$C + H_2 \rightarrow CH + H \qquad \sim 10^{-5}$$
$$CH + H_2O \rightarrow CH_2OH \qquad \sim 10^{-3}$$
$$CH_2OH + H \rightarrow CH_2O + H_2 \qquad \sim 10^{-4}$$
$$CH_2O + H \rightarrow HCO + H_2 \qquad \sim 10^{-4}$$
$$HCO + H \rightarrow CO + H_2 \qquad \sim 10^{-5}$$

Such short chemical loss timescales imply that CO is reformed from H_2O much more rapidly than CO is photolyzed, and so preservation of a self-shielding derived isotope anomaly is unlikely. However, 2000 K and 10 mbar may not be representative of the inner solar nebula. These calculations will be repeated for 1500 K and 0.1 mbar and the results presented.

CO self-shielding in the outer solar nebula: Self-shielding in the outer solar nebula is similar to that in molecular clouds (e.g., [8]). At temperatures < 120 K (approximately) reactions on grain surfaces involving H atoms and O atoms produced during CO photolysis yield ^{16}O-depleted H_2O. The low temperatures inhibit isotopic equilibration of residual CO and H_2O. Incorporating CO photolysis and self-shielding into a photochemical model for the solar nebula [4] yields the 3-isotope results for total nebular water shown in Figure 1. These results are for a distance R = 30 AU, Z = 0 (nebula midplane), a turbulent viscosity parameter $\alpha = 10^{-2}$, and a FUV flux = 500 times the local interstellar medium flux, all of which are plausible parameter values. Inclusion of differential absorption by H_2 reduces the slope of the trajectory shown in Fig. 1 from 1.1 to about 1.0, making the model calculations consistent with measurements of CAI slopes [9,10].



The timescale required for total nebular water to reach the isotopic values inferred from Murchison [2,11] is ~ 10^5 years, which is comparable to the radial transport timescale inward from 30 AU. The implications of these fairly long timescales will be discussed.

References: [1] Clayton R. N. (2002) *LPSC XXXIII,* abstract #1326. [2] Clayton R. N. and Mayeda T. K. (1984) *Earth Planet. Sci. Lett., 67,* 151-161. [3] Yurimoto, H. and Kuramoto, K. (2004) *Science 305*, 1763-1766. [4] Lyons J. R. and Young E. D. (2005), *Nature*, 435, 317-320. [5] Hashizume K. and Chaussidon M. (2005) *Nature*, 434, 619. [6] Lyons, J. R. and Young, E. D. (2003), *LPSC XXXIV*, abs. #1981. [7] Navon O. and Wasserburg G. J. (1985), *Earth Planet. Sci. Lett. 73*, 1-16. [8] van Dishoeck E. and Black J. (1988) *Astrophys. J. 334*, 771-802. [9] Clayton, R. N. (1993), *Ann. Rev. Earth Space Sci. 21*, 115-149. [10] Young, E. D. and Russell, S. S. (1998) *Science 282*, 452-455. [11] Young E. D. (2000) *Phil. Trans. Roy. Soc. Lond. 359*, 2095-2110.

MASS-INDEPENDENT GAS PHASE AND SURFACE REACTIONS OF GEOCHEMICAL AND COSMOCHEMICAL INTEREST. R. A. Marcus[1], [1]Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA; ram@caltech.edu.

Introduction: The unusual "mass-independent" oxygen isotope effect in stratospheric ozone [1] and in calcium aluminum enriched inclusions (CAIs) in chondritic meteorites [2] has aroused much interest. This effect, in which the ^{17}O and ^{18}O show equal fractionation, poses interesting challenges to experimentalists, theorists, and their interaction.

The stratospheric formation of ozone involves $O + O_2 \leftrightarrow O_3^*$, followed by $O_3^* + M \rightarrow O_3 + M$, where O_3^* is vibrationally excited and M is a third body. A non-RRKM explanation (non-statistical distribution of vibrational states) has been proposed for the O_3 phenomenon [3]: At the usuial isotopic ocmpositions only the ^{17}O and ^{18}O can form isotopically asymmetric ozone molecules, and for dynamical reasons they live longer than the symmetric isotopomers [3]. So, collisional sstabilization of isotopically asymmetric ^{17}O and ^{18}O ozones occurs preferentially relative to symmetric ozones, yielding the mass-independent enhancement. (References to the statistical (RRKM, Rice, Ramsperger, Kassel, Marcus) theory of unimolecular reactions and bimolecular recombinations are found in [3], in which the present non-RRKM effect is also discussed.)

The CAIs, the earliest processed solids in the solar system, were formed instead some 4.56 billion years ago. CAIs, such as $(MgO)(Al_2O_3)_3$ and $(MgO)_2SiO_2$, are believed to have formed at 1500-2000 K and 10^{-3} to 10^{-4} atm.

Proposed mechanism and Discussion:

A possible chemical mechanism for CAI formation [4] involves the surface analogue of the O_3 phenomenon, with surface reactions leading to the vibrationally excited adsorbed species XO_2^*(ads), as in $XO(ads) + O(ads) \leftrightarrow XO_2^*(ads)$, where X = Si,Al,.. . Calculations and other data show that this O(ads) would form principally from H_2O + surface → H_2 + O(ads), rather than from O + surface → O(ads) [4]. The surface of a growing grain has an entropic effect of many orders of magnitude on the position of the monoxide-dioxide equilibrium relative to the gas phase equilibrium by acting as a concentrator. A gas phase non-RRKM effect for ozone cannot apply to gas phase precursors of CAIs for two reasons, the rarity of the 3-body collisions at low pressures of M, and the H_2 and H attack dioxides. So a surface reaction is required instead for the desired fractionation.

If a surface non-RRKM effect exists, it would yield XO_2^*(ads) that is mass-independently rich in ^{17}O and ^{18}O, and O(ads) and XO(ads) that are mass-independently poor in ^{17}O and ^{18}O. The ^{16}O-depleted XO_2^*(ads) is then lost to the gas phase, directly or after vibrational energy loss to the grain. It leaves the solid by evaporation or upon attack by a gas phase reductant. These XO_2^*(ads) have a ballpark estimated natural lifetime toward dissociation of 500 fs at 2000 K. The other species, O(ads) and XO(ads), are ^{16}O-enriched and react with Ca(ads) and other adsorbed metal atoms or metallic oxides to form ^{16}O-enriched CAIs. There is a competition between the loss of XO_2^*(ads) (or XO_2(ads)) to the gas phase versus the incorporation of the XO, O, Ca, Mg and other species into the lattice to form the CAIs.(X=Si,Al..)

One feature of this chemical mechanism for the oxygen isotope anomaly is that only one oxygen isotope reservoir is required in the solar nebula. It also does not require a sequestering of intermediate products which could undergo isotopic exchange, hence undoing the original isotopic fractionations.

While there are many indirect experimental tests of the mechanism proposed for isotope effects in ozone formation [3], direct tests, such as pump-dump laser excitation of O_3 and a search for non-single exponential dissociation decay of O_3^*, are so far absent. The more difficult study of the existence of a non-RRKM effect on a solid phase (or melt) would be desirable using a source of SiO and of H_2O (or O), and other atoms such as Ca and Al.

The study of the rate of dissociation of a mineral is easier than of its rate of formation by condensation from its components from the gas phase. The interesting question of whether a chemical mechanism for the CAIs isotope effect could also lead to a mass-independent fractionation in the dissociation of a mineral will be discussed. It would require two dissociation modes, one leading from XO_2^*(ads) and the other from O(ads) + XO(ads) in the assumed XO (ads) + O (ads) ↔ XO_2^* (ads) pre-equilibrium. Each mode would have its own isotopic composition, and a separate trapping of each set of products would be needed to avoid their subsequent mixing XO_2^* (ads). The difference in adsorbed O_3^* and XO_2^* is also discussed. Mass-independent fractionation poses new challenges in both gas phase and surface studies.

References:[1] Thiemens M. H. and Heidenreich J. E. (1983) *Science* 219, 1073. [2] Clayton R. N., Grossman L., Mayeda T. K. (1973) *Science* 182, 485 [3] Gao Y. Q. and Marcus R. A. (2002) *J. Chem. Phys.* 110, 137. [4] Marcus R. A. (2004) *J. ibid* 121, 8201.

THE FORMATION AND PROCESSING OF INTERSTELLAR OXYGEN-RICH DUST. F. Markwick-Kemper, Department of Astronomy, PO Box 3818, University of Virginia. Charlottesville, VA 22903-0818, Ciska@virginia.edu.

Introduction: By means of spectroscopic observations in the infrared it is possible to study the mineralogical composition and grain properties of dust grains in interstellar and circumstellar environments. In particular the spectrographs mounted on space telescopes such as the Infrared Space Observatory [1,2] and the Spitzer Space Telescope [3,4] have enabled us to study the composition and dust properties in great detail. In this talk, I will provide an overview of what is known about the formation and evolution of oxygen-rich dust species.

The life cycle of dust: Oxygen-rich dust is formed in the outflow of evolved stars, which have exhausted hydrogen core burning. The main dust factories are the so-called Asymptotic Giant Branch stars, which have developed a dense stellar wind in which the conditions are suitable for the formation of dust. This environment is relatively sheltered from energetic radiation, and the newly formed dust shows an amazing variety of properties and compositions, including a relatively high degree of crystallinity [5,6]. In the interstellar medium, the main depletion sink of oxygen in the interstellar medium is in the form of amorphous silicates, e.g. [8]. In this talk, I will discuss the differences between the circumstellar and interstellar environments, and give an overview of the processes that drive the evolution of the oxygen-rich dust properties.

References:

[1] Kessler, M. F. et al. 1996, *Astron. Astrophys.* 315, L27. [2] de Graauw, T. et al. 1996, *Astron. Astrophys.* 315, L49. [3] Werner, M. W. et al. 2004, *Astrophys. J. Suppl.* 154, 1. [4] Houck, J. R. et al. 2004, *Astrophys. J. Suppl.* 154, 18. [5] Molster, F. J. and Waters, L. B. F. M., 2003, in *Astromineralogy*, ed. T. K. Henning, Lecture Notes in Physics, vol. 609, p. 121-170. [6] Molster, F. J. and Kemper, F. 2005, in *ISO science legacy – a compact review of ISO major achievements*, eds. C. Cesarsky and A. Salama, publ. Springer, *in press.* [7] Kemper, F., Vriend W. J., and Tielens, A. G. G. M. 2004, *Astrophys. J.* 609, 826.

OXYGEN ISOTOPIC INSIGHTS INTO ORIGINS AND HISTORIES OF COMETARY MATERIALS. S. Messenger and L. P. Keller, NASA Johnson Space Center, Astromaterials Research & Exploration Science Division, Robert M Walker Laboratory for Space Science, Houston TX 77058.

Introduction: Originating from the coldest and most quiescent portions of the solar system, comets are likely to be the least processed remnants of the solar nebula. Though once considered to be unprocessed assemblages of interstellar materials, a minor population of crystalline silicates is apparent in some cometary spectra, suggesting that they contain materials processed at high temperatures [1].

Chondritic porous (CP) interplanetary dust particles (IDPs) bear similarities to cometary dust, including their fine grain sizes, fragile microstructures, high abundances of volatile elements and carbon, and anhydrous mineralogy. Infrared spectra of CP IDPs are also a remarkably good match to comets [2]. CP IDPs have been dynamically linked with comets from their high atmospheric entry velocities inferred from thermal release measurements of solar wind He [3].

Here we summarize constraints on the origins of cometary grains derived from oxygen isotopic measurements of submicrometer grains in CP IDPs, acquired with the Washington University NanoSIMS 50 ion microprobe.

Presolar Grains: Circumstellar silicates and oxides have been found in both meteorites and IDPs [e.g. 4-6]. These grains have highly non-solar isotopic compositions, with $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios varying by more than 2 orders of magnitude. Most grains apparently derive from red giant and asymptotic giant branch stars, with a minor (~1 %) population from supernovae [7]. Of the few presolar silicates whose mineralogy has been definitively identified by TEM, 4 are amorphous silicates including GEMS grains, and 2 are olivine grains. The mineralogy of presolar silicates is distinctly different from interstellar silicates, that appear to be dominated by amorphous grains.

Silicate stardust grains ARE more abundant in some CP IDPs (450 – 5,500 ppm; 4,8) than in meteorites (<180 ppm; 5,6). Nonetheless, these IDPs are clearly dominated (>99 %) by grains with O isotopic compositions that are so far indistinguishable (within ~50‰) from solar.

Isotopically Solar Crystalline Grains: Crystalline oxides and Mg-rich silicates are common components of CP IDPs. The mineralogy and microstructure of these grains are consistent with condensation from a high T (>1,300 K) gas. Most (>95 %) such grains studied so far have solar O isotopic compositions. It is very likely that most such grains originated in the solar system itself because (1) most oxides and silicates formed around evolved stars have distinctly non-solar O isotopic compositions and (2) crystalline silicates are extremely rare in the interstellar medium (<0.2% of interstellar silicates; 9). These grains probably formed in the inner, warmer regions of the solar nebula, and were transported to the Kuiper belt by turbulence or perhaps the X-wind [10,11].

Isotopically Solar Amorphous Silicates: Amorphous silicates are a major component of CP IDPs, including GEMS grains [12] and other glassy grains. GEMS grains are proposed to have been produced by extensive, gradual sputtering and re-condensation of materials in the ISM [12], a process that would tend to homogenize their chemical and isotopic compositions. Alternatively, these grains may have been late-stage nebular condensates [13], also naturally leaving the grains with solar isotopic compositions.

Because circumstellar silicates tend to have strongly non-solar O isotopic compositions, many interstellar grains will retain distinct isotopic compositions despite extensive mixing with isotopically solar interstellar gas. Among the 1,000 submicrometer grains measured in IDPs so far, less than 1% differ from solar O isotopic composition by more than 50 ‰. If these grains originally had O isotopic compositions similar to circumstellar oxides, their present O isotopic compositions indicate that most of them must have been *thoroughly* homogenized, containing less than 5% of the original stellar condensate. Higher precision O isotopic measurements will be required to identify the expected partially homogenized interstellar silicates that should be marked by moderately anomalous (50 – 100 ‰) isotopic compositions.

References: [1] Crovisier J. et al. (2000) ASP Conf. Ser. 196, 109-117. [2] Bradley J. P. et al. (1999) *Science* **285**, 1716. [3] Joswiak D.J. *et al*. (2000) LPS 31, #1500. [4] S. Messenger, L. P. Keller, F. J. Stadermann, R. M. Walker, E. Zinner *Science* **300**, 105 (2003). [5] A. Nguyen & E. Zinner, *Science* **303**, 1496 (2004) [6] Mostefaoui S. & Hoppe P. (2004) *ApJ* **613**, L149. [7] Messenger S., Keller L.P., & Lauretta D.S. (2005) Science, *in press* [8] Floss C. & Stadermann F.J. (2004) LPS 35, #1281. [9] Kemper F. *et al*. (2001) ApJ 369, 132 [10] Bockelee-Morvan *et al*. (2002) **384**, 1107 [11] Shu F. et al. (2001) ApJ 548, 1029 [12] Bradley, J. P. and Dai, Z. (2004) *ApJ*, **617**, 650. [13] Keller L.P. & Messenger S. (2005) Proc. Chondrites Protoplanetary Disk.

NUCLEOSYNTHESIS AND GALACTIC CHEMICAL EVOLUTION OF THE ISOTOPES OF OXYGEN.
B. S. Meyer, Department of Physics and Astronomy, Clemson University, Clemson, SC 29634-0978, USA (mbradle@clemson.edu).

Introduction: The stable isotopes of oxygen are important diagnostics of stellar nucleosynthesis and Galactic chemical evolution. This is primarily due to the fact that ^{16}O is a principal product of stellar evolution and is therefore very abundant in the Galaxy. It is also due to the fact that ^{16}O is a primary isotope while ^{17}O and ^{18}O are secondary isotopes.

Nucleosynthesis: ^{16}O is primarily produced at the end of helium burning in stars. ^{12}C produced by the triple-alpha reaction captures another ^{4}He to produce ^{16}O. This means that the interplay of the triple-alpha reaction and ^{12}C(alpha,gamma)^{16}O determines the ratio of ^{12}C to ^{16}O in the star after helium burning, which, in turn, governs the subsequent stellar evolution (e.g., [1]). Experimental determination of the ^{12}C(alpha,gamma)^{16}O reaction rate is difficult and is the subject of intense study (e.g., [2]). ^{16}O abundance is increased further during neon burning. Because ^{16}O can be produced by stars initially composed only of hydrogen, it is a primary isotope. It is worth noting that ^{16}O is, in fact, one of the dominant products of massive stars. For example, one may consider a model of a star 25 times the mass of the Sun [3]. This model began with about 0.23 solar masses of ^{16}O but ejected 3.24 solar masses of that isotope.

By contrast, ^{17}O and ^{18}O are secondary isotopes, which means their production requires pre-existing seed nuclei. ^{17}O is dominantly produced by CNO burning of hydrogen into helium and is thus a prevalent isotope in hydrogen burning shells in stars. ^{18}O is primarily made when abundant ^{14}N, left over from CNO burning, captures ^{4}He. This means ^{18}O is abundant in helium-rich zones in stars. Because ^{16}O and ^{18}O production requires helium burning while ^{17}O only requires hydrogen burning, low-mass stars may contribute more significantly to the synthesis of ^{17}O than to ^{16}O or ^{18}O.

Galactic Chemical Evolution: Since ^{16}O is a primary isotope, it was produced in the first generation of stars. Observations of very metal-poor stars show the rise of oxygen with metallicity in the early Galaxy (e.g., [4]). The primary nature of the nucleosynthesis of ^{16}O means that this rise is roughly linear in time. By contrast, the secondary nucleosynthesis of ^{17}O and ^{18}O means that the abundance of these isotopes in the Galaxy will rise roughly quadratically with time in a chemical evolution model (e.g., [5]). Such evolution is evident in Figure 1, which shows the evolution of the mass fraction of the oxygen isotopes in the interstellar medium from a standard Galactic chemical evolution model. The figure was generated with the Clemson University online Galactic Chemical Evolution code available at the web site

http://nucleo.ces.clemson.edu/home/online_tools

Interested readers are invited to explore the details of stellar yields and Galactic chemical evolution of the oxygen isotopes with this tool.

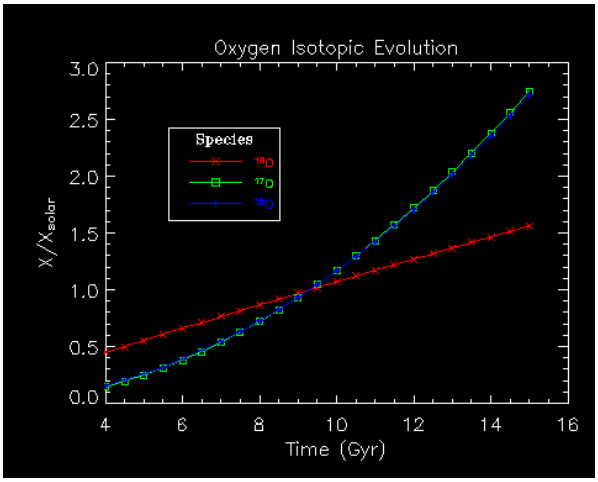


Figure 1: Chemical evolution of the mass fractions of the oxygen isotopes relative to their solar values in the interstellar medium in a standard chemical evolution model. The ^{16}O mass fraction rises linearly with time because it is a primary isotope. ^{17}O and ^{18}O rise quadratically with time because they are secondary isotopes. This figure was generated with the Clemson University online Galactic Chemical Evolution code.

References: [1] El Eid M. F. et al. (2004) *Astrophys. J.*, *611*, 452-465. [2] Kunz R. et al. (2002) *Astrophys. J., 567,* 643-650. Meyer B. S. et al. (1995) *Meteoritics, 30*, 325-334. [4] Israelian G. et al. (2001) *Astrophys. J, 551*, 833-851. [5] Clayton D. D. (1988) *Astrophys. J., 334,* 191-195.

Presolar O-Rich Dust Grains In The Solar System. L. R. Nittler[1], [1]Carnegie Institution of Washington, Washington DC, 20015, USA, email: lrn@dtm.ciw.edu.

The bulk solar system composition represents a mixture of materials that were formed or processed through countless numbers of individual stars in the billions of years of presolar galactic history. Although most of the pre-existing dust grains were vaporized and their atoms homogenized with the solar nebula gas during early stages of solar system formation, a small fraction of presolar dust survived in the matrix of primitive meteorites and in interplanetary dust particles (IDPs). These grains are recognized as presolar stardust on the basis of highly unusual isotopic compositions, compared to other materials found in the Solar System. These isotopic compositions reflect the stellar gases from which they condensed and provide information about a wide array of astrophysical processes [1-3]. This talk will review the subset of known presolar grains that are O-rich, including both silicate and oxide phases.

O isotopic ratios for the known presolar O-rich grains are shown in the Figure. More than 600 presolar oxide grains (including Al_2O_3, $(Mg,Fe)(Al,Cr)_2O_4$, $CaAl_{12}O_{19}$, TiO_2, and $FeCr_2O_4$) and more than 60 presolar silicate grains (including olivine, pyroxene and glass) have now been reported from meteorites and IDPs [4-10]. In addition to O isotopes, Mg isotopes have been measured in many grains, Ti and/or Ca isotopes in a few oxides and Si isotopes in a few silicates.

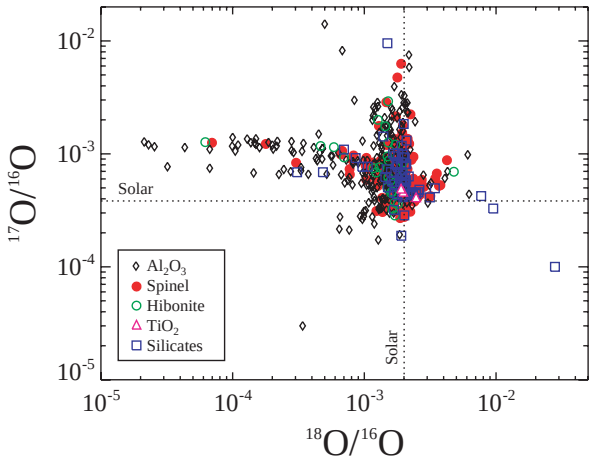
The observed isotopic signatures point to a diversity of stellar sources. The majority of grains are enriched in ^{17}O and depleted in ^{18}O, relative to Solar – a signature of H burning by the CNO cycle. Most of these grains are believed to have formed in low-mass asymptotic giant branch (AGB) stars, in agreement with astronomical estimates that AGB stars dominate the production of O rich stardust in the Galaxy [11]. The large ^{18}O depletions and high inferred $^{26}Al/^{27}Al$ ratios of a fraction of ^{17}O-rich grains ($^{18}O/^{16}O < 10^{-3}$) point to non-standard mixing in their parent stars [12]. A supernova origin is likely for a few grains, including the grains with the lowest $^{17}O/^{16}O$ and/or highest $^{18}O/^{16}O$ ratios [6, 13, 14]. The rarity of such grains indicates that supernovae did not dominate the production of O-rich dust in the interstellar medium from which the Sun formed.

The mineralogy and microstructures of presolar grains provide information about stellar dust formation processes and help to interpret infrared spectra of dusty stars. For example, presolar Al_2O_3 is found both in the crystalline corundum structure and in an amorphous form [15], consistent with infrared evidence that both forms are present in some O-rich AGB stars. Both crystalline and amorphous grains have been found among the presolar silicates. However, both the ratio of crystalline to amorphous grains and the iron contents appear to be higher in the meteoritic grains compared to astronomical observations of circumstellar and interstellar silicates. The data are limited, however, and silicates are likely to be more sensitive to parent body effects than more resistant phases like Al_2O_3.

Note that the average composition of the presolar grains is enriched in ^{17}O and depleted in ^{18}O, relative to the bulk Solar System. Since the grains probably represent a reasonably representative sample of stellar sources of O-rich dust, this indicates that most of the O in the Solar System originally was expelled from stars (primarily supernovae) in gaseous form.

References:

[1] Nittler L. R. (2003) *EPSL, 209,* 259-273. [2] Clayton D. D. and Nittler L. R. (2004) *ARAA, 42,* 39-78. [3] Zinner E. (1998) *AREPS, 26,* 147-188. [4] Huss G. R., et al. (1994) *ApJ, 430,* L81-84. [5] Nittler L., et al. (1997) *ApJ, 483,* 475-495. [6] Choi B.-G., et al. (1998) *Science, 282,* 1282-1289. [7] Messenger S., et al. (2003) *Science, 300,* 105-108. [8] Zinner E., et al. (2003) *GCA, 67,* 5083-5095. [9] Nguyen A. N. and Zinner E. (2004) *Science, 303,* 1496-1499. [10] Mostefaoui S. and Hoppe P. (2004) *ApJ, 613,* L149-L152. [11] Kemper F., et al. (2004) *ApJ, 609,* 826-837. [12] Nollett K. M., et al. (2003) *ApJ, 582,* 1036-1058. [13] Nittler L. R., et al. (1998) *Nature, 393,* 222. [14] Messenger S., et al. (2005) *Science,* 1109602. [15] Stroud R. M., et al. (2004) *Science, 305,* 1455-1457.



The Interstellar Heritage of Cometary Composition

Scott Sandford, NASA-Ames Research Center, Astrophysics Branch, Moffett Field, CA 94025 USA

Phone: 650-604-6849
Fax: 650-604-6779
Email: ssandford@mail.arc.nasa.gov

It is a generally held belief that comets represent objects that contain significant amounts of material that experienced relatively little alteration during cometary formation in the solar nebula, and that these materials subsequently suffered very little parent body alteration afterwards. If this is the case, then comets should represent a reservoir of unaltered, or only slightly altered, interstellar materials. Comparison of the volatile icy components of dense molecular clouds with the composition of cometary ices as inferred from remote observations of the gas phase species in cometary comae are consistent with this possibility; the same molecular species are seen to dominate in both. Thus, the oxygen inventory of cometary volatiles may have a very direct relationship to the oxygen contents of interstellar volatiles, with the main carriers being molecules like H_2O, CO, CO_2, and CH_3OH. Deuterium and ^{15}N isotopic studies of IDPs suggest a similar relationship may also exist for some organic materials, although the oxygen contents of these materials are less well defined. The talk will explore some of the abundance and isotopic implications that are implied by a close genetic relationship of cometary and interstellar volatiles. The inter-relationship of interstellar and cometary O carriers in more refractory phases may be more complex, since interstellar silicates are thought to be dominated by amorphous silicates, while cometary silicates appear to contain both amorphous and crystalline silicates.

VALENCE OF Ti AND V IN FASSAITE: A RECORDER OF OXYGEN FUGACITY DURING CRYSTALLIZATION OF COARSE-GRAINED REFRACTORY INCLUSIONS. S. B. Simon[1], S. R. Sutton[1,2], and L. Grossman[1,3]. [1]Dept. Geophysical Sci., 5734 S. Ellis Ave.; [2]Consortium for Advanced Radiation Sources; [3]Enrico Fermi Institute, 5640 S. Ellis Ave., The University of Chicago, Chicago, IL 60637, USA (sbs8@midway.uchicago.edu).

Introduction. Fassaite (Ti-, Al-rich clinopyroxene [1]) is a major phase in Type B (pyroxene-rich), coarse-grained refractory inclusions, which are found in CV3 carbonaceous chondrites. Both Ti and V are compatible in this phase during fractional crystallization of inclusion melts, and both have two valence states that are stable at the oxygen fugacity of the solar nebula, ~7 log units below the iron-wüstite buffer. This makes fassaite a potential recorder of f_{O_2} that can tell us whether inclusions crystallized in a solar gas. The Ti^{3+}/Ti^{4+} ratio of fassaite can be calculated from electron probe (EMP) analyses assuming stoichiometry [2] and it can be measured directly by X-ray absorption near edge structure (XANES) spectroscopy. Measurement of V^{2+}/V^{3+} ratios in fassaite requires XANES.

Typically V_2O_3, Sc_2O_3 and total Ti oxides (TiO_2 + Ti_2O_3) decrease from core to rim in Type B fassaite [3]. The Ti^{3+}/Ti^{4+} ratio commonly decreases from core to rim in fassaite in Type B1 (having a melilite-rich mantle) inclusions but not in fassaite in Type B2 (no mantle) inclusions. Also, Type B1 fassaites commonly exhibit sharp increases, or "spikes", in their Ti and V contents and their Ti^{3+}/Ti^{4+} ratios but not in Sc or rare earth element contents [4], which seems to rule out a simple change in crystallization assemblage, such as incoming of anorthite, as the cause of the spikes. As the only affected elements are the two with multiple valence states, a redox change is suggested. To investigate this feature we have measured the Ti^{3+}/Ti^{4+} and V^{2+}/V^{3+} ratios in fassaite in a Type B1 and a Type B2 inclusion from Allende.

Methods. Major element zoning and Ti oxidation state were documented by EMP, and abundances and valence states of Ti and V were determined by XANES. As in [5], with a 5 μm X-ray beam, XANES spectra were measured over the V K pre-edge peak (~5468 eV) from 5450 to 5500, with additional normalization measurements at 5600 eV. Analogous measurements were made over the Ti K pre-edge peak, at 4969 eV. By comparing the spectra to those for pure oxidation state standards, we determined oxidation states for each analysis spot, reported as values between 3 and 4 for Ti and between 2 and 3 for V.

Results. EMP and XANES traverses were conducted across two spikes in TS34 (B1) and across two grains in TS21 (B2). XANES results agree with EMP data, which show sharp increases in Ti (e. g., in one grain in TS34, from 3.57 to 5.10 wt%) and V (0.03 to 0.12 wt%) oxide contents and in Ti^{3+}/Ti^{4+} at the spike. In that grain, the Ti oxidation state drops from a pre-spike value of 3.54±0.05 (i.e., $Ti^{3+}\approx Ti^{4+}$) to 3.14±0.11 ($Ti^{3+}>>Ti^{4+}$). Surprisingly, across the same spike, we did not detect a change in V valence, with measurements of 2.51±0.03 pre-spike and 2.49±0.08 at the spike. In Type B2 inclusions, fassaite Ti^{3+}/Ti^{4+} ratios are within the range of those of Type B1 fassaites, and the V valence in two B2 fassaite crystals we analyzed averages 2.40±0.09 and 2.52±0.09, within error of the results for the two B1 grains, 2.39±0.08 and 2.42±0.10. These results are clear evidence for the presence of V^{2+} in both Type B1s and B2s, with $V^{2+}\approx V^{3+}$.

Discussion. The measured Ti^{3+}/Ti^{4+} and V^{2+}/V^{3+} ratios are consistent with crystallization from a liquid in equilibrium with a gas of solar composition. Fassaite favors Ti^{3+} over Ti^{4+} [2] so fractional crystallization can cause the Ti^{3+}/Ti^{4+} ratio to decrease from core to rim in a crystal, but only if the residual liquid is isolated from the nebular gas and prevented from reequilibrating. This seems to have occurred in the B1s but not in the B2s. Many late B1 liquids had low Ti^{3+}/Ti^{4+} but were exposed to the nebular gas before completion of crystallization, causing reequilibration and sharp increases in Ti^{3+}/Ti^{4+} of crystallizing pyroxene. The V^{2+}/V^{3+} ratio of the residual liquid should have behaved similarly, in which case the spikes in V contents would imply that V^{2+} is more compatible in fassaite than V^{3+}. This scenario is feasible, as V^{2+} can enter the pyroxene M1 or M2 site and does not require a coupled substitution for charge balance, but experiments are needed for confirmation. If $D_{V2+}>D_{V3+}$, it is unclear why a change in the V oxidation state at the concentration spike was not detected. One possibility is that the V valence in the fassaite reequilibrated by subsolidus charge transfer with relatively abundant Ti.

References: [1] Dowty E. and Clark J. (1973) *Am. Min. 58,* 230-242. [2] Beckett J. (1986) Ph. D. dissert. U. Chicago. [3] Simon S. et al. (1991) *GCA 55,* 2635-2655. [4] Simon S. et al. (1992) *Meteoritics* 27, 289-290. [5] Sutton S. et al. (2002) *LPS XXXIII,* Abstract #1907.

OXYGEN IN THE DIFFUSE INTERSTELLAR MEDIUM. Theodore P. Snow and Adam G. Jensen, University of Colorado (CASA - University of Colorado, 389 UCB, Boulder, CO 80309-0389; tsnow@casa.colorado.edu).

Oxygen is observed in the interstellar medium in lines of sight sufficient optically thin to allow measurements of ultraviolet absorption lines of the neutral atom, O I, which is the dominant ionization stage in diffuse and dense clouds. Starting with the *Copernicus* satellite in the 1970s, there is now an extensive archive of O I measurements, for clouds with visual dust extinctions ranging from 0 to 5 magnitudes. The *Cosmic Origins Spectrograph*, to be installed aboard the Hubble Space Telescope in 2007, will extend this range to Av = 10 magnitudes or more.

In this paper we describe the observations of UV O I lines and summarize the results to date. We address the gas-phase abundance of oxygen in the diffuse ISM and its dependence on local physical conditions; the question of the standard oxygen abundance to be used in assessing the depletion of oxygen from the gas onto dust grains; and the constraints on the oxygen content of the dust. We will discuss the question of whether the fraction of oxygen stored in interstellar dust increases with increasing cloud density, and whether enhanced depletion onto dust might occur during the early stages of star formation. We conclude with a summary of the important remaining issues regarding interstellar oxygen and its relationship to oxygen in the solar system.

Oxygen and Other Volatiles in Jupiter: Insights into the Early Solar System.

Michael H. Wong[1], Sushil K. Atreya[2], and Paul R. Mahaffy[3].

1: Ast
Oceanic, and Space Sciences, University of Michigan. 3: Laboratory for Atmospheres, Code 915, NASA Goddard Space Flight Center.

Workshop on Oxygen in the Earliest Solar System. 19–22 September 2005, Gatlinburg TN.

Introduction

Water is the primary oxygen-bearing species in Jupiter's atmosphere, but its bulk abundance in the planet has probably not yet been measured. Oxygen and the other volatiles were brought to Jupiter's atmosphere via planetesimal accretion, so these elements provide insight into the properties of the planetesimal diet consumed by the young Jupiter.

Measurements of Jupiter's volatiles

The Galileo Probe Mass Spectrometer (GPMS) provided the deepest available measurement of the water mixing ratio in Jupiter [1,2]. Water mixing ratios are shown in Fig. 1 for the 10–12 bar and 17–21 bar ranges. For a hypothetical well-mixed Jupiter atmosphere with a solar abundance of H_2O, the cloud base would be near 5 bar, and a uniform mixing ratio would be expected below that level. However, the probe descended into a 5-μm hotspot and measured volatile abundances depleted by local meteorological effects. The condensible gases (NH_3, H_2S, and H_2O) were seen to increase with depth, and it is impossible to determine based on the available data whether the deep H_2O mixing ratio was sampled. Examples of attempts to infer the deep oxygen abundance by a wave propagation model [3], CO measurements [4], or infrared spectroscopic water retrievals [5] have not been conclusive.

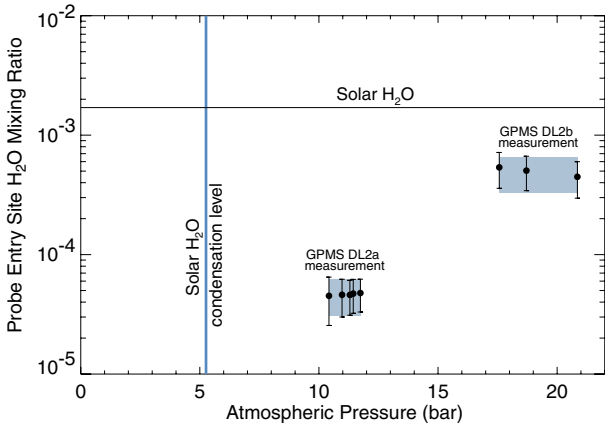


Figure 1. The GPMS measurements of water near 11 and 20 bar [2] in the probe entry site.

The GPMS measurements of CH_4, NH_3, and H_2S (Fig. 2) were successful at determining bulk abundances of these species in Jupiter's atmosphere, and the CH_4 and NH_3 results are in good agreement with independent spectroscopic determinations [8,9,10], while the H_2S mixing ratio was uniquely measured by the GPMS.

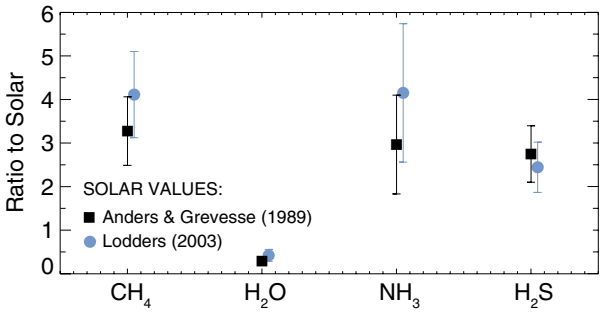


Figure 2. Ratios of GPMS measurements of volatile gases [2] to protosolar abundances [6,7].

Implications for giant planet formation

The enriched volatiles (Fig. 2) and noble gases in Jupiter were delivered by accreted planetesimals, with candidate compositions such as amorphous ice formed at T ≤ 30 K [11], crystalline ice with volatiles trapped in clathrates [12,13], and "tarry" carbonaceous material [14]. Both icy planetesimal scenarios require large water enrichments, whereas Lodders [14] cannot place any constraints on water or nitrogen abundances, so an accurate determination of Jupiter's oxygen abundance is needed to distinguish between candidate planetesimal compositions.

References

[1] Niemann, H.B., Atreya, S.K., Carignan, G.R., Donahue, T.M., Haberman, J.A., Harpold, D.N., Hartle, R.E., Hunten, D.M., Kasprzak, W.T., Mahaffy, P.R., Owen, T.C., Way, S.H., 1998. *J. Geophys. Res.* 103, 22,831–22,846. [2] Wong, M.H., Mahaffy, P.R., Atreya, S.K., Niemann, H.B., Owen, T.C., 2004. *Icarus* 171, 153–170. [3] Ingersoll, A. P. and Kanamori, H., 1995. *Nature* 374, 706–708. [4] Bézard, B., Lellouch, E., Strobel, D., Maillard, J., and Drossart, P., 2002. *Icarus* 159, 95–111. [5] Bjoraker, G.L., Larson, H.P., Kunde, V.G., 1986. *Icarus* 66, 579–609. [6] Anders, E., Grevesse, N., 1989. *Geochim. Cosmochim. Acta* 53, 197–214. [7] Lodders, K., 2003. *Astrophys. J.* 591, 1220–1247. [8] Gautier, D., Bézard, B., Marten, A., Baluteau, J.P., Scott, N., Chedin, A., Kunde, V., Hanel, R., 1982. *Astrophys. J.* 257, 901–912. [9] Knacke, R.F., Kim, S.J., Ridgway, S.T., Tokunaga, A.T., 1982. *Astrophys. J.* 262, 388–395. [10] Folkner, W.M., Woo, R., Nandi, S., 1998. *J. Geophys. Res.* 103, 22847–22856. [11] Owen, T., MahaJy, P., Niemann, H.B., Atreya, S., Donahue, A., de Pater, I., 1999. *Nature* 402, 269. [12] Gautier, D., Hersant, F., Mousis, O., Lunine, J.I., 2001. *Astrophys. J.* 550, L227. Erratum. Astrophys. J. 559, L183. [13] Hersant, F., Gautier, D., and Lunine, J. I., 2004. *Planet. Space Sci.* 52, 623–641. [14] Lodders, K., 2004. *Astrophys. J.* 611, 587–597.

H_2O TRANSPORT AND $\Delta^{17}O$ IN THE SOLAR NEBULA. E.D. Young[1], [1]Department of Earth and Space Sciences and Institute of Geophysics and Planetary Physics, University of California Los Angeles, 2676 Geology Building, Los Angeles, CA 90095 (eyoung@ess.ucla.edu).

Introduction: Recent theoretical studies suggest that the inner solar nebula became enriched in H_2O with time by inward transport and sublimation of water ice [1]. At least two proposed means for producing non-mass dependent oxygen isotope effects ($\Delta^{17}O \neq 0$) in the nebula, photolysis of CO at disk surfaces accompanied by shielding of FUV light by CO and H_2 [2, 3] and a grain surface-mediated chemical η effect [4], suggest a direct link between [H_2O] and $\Delta^{17}O$. The link provides testable predictions.

Oxygen fugacity: A rise in the number density of H_2O in the vapor phase should have resulted in a general correlation between the fugacity of oxygen (calculated fO_2 is a proxy for [O]) and $\Delta^{17}O$ in inner solar system materials. To the extent that CAIs, generally the most ^{16}O-rich objects in the solar system, are also among the most reduced rocks [5], the prediction appears to be born out by the data. The [O] associated with changing $\Delta^{17}O$ has clear implications for the η effect [4] as well as for the purported links with [H_2O] [2].

Total gas $\Delta^{17}O$: In order to constrain the original isotopic composition of the inner solar system gas one needs an estimate of the fraction of oxygen that was bound as rock-forming dust relative to the fraction of oxygen that was in the gas. The relevant steady-state mass-balance equation is

$$\delta^{\mathrm{f}}_{\mathrm{gas}} - \delta^{\mathrm{o}}_{\mathrm{gas}} = \frac{x_{\mathrm{rx}}}{1 - x_{\mathrm{rx}}}(\delta^{\mathrm{o}}_{\mathrm{rx}} - \delta^{\mathrm{f}}_{\mathrm{rx}}) = F\,(\delta^{\mathrm{o}}_{\mathrm{rx}} - \delta^{\mathrm{f}}_{\mathrm{rx}}) \quad (1)$$

where $^{\mathrm{o}}$ refers to the initial condition, $^{\mathrm{f}}$ refers to the final condition, δ is the oxygen isotope ratio of interest in per mil, x_{rx} is the fraction of oxygen bound to rock-forming elements, and x_{gas} is the oxygen fraction in the gas phase. With revised solar abundances F = 0.36. Taking $\delta^{\mathrm{o}}_{\mathrm{rx}} = -50$ ‰ for both $\delta^{17}O$ and $\delta^{18}O$ [6], and assuming the oxygen isotopic compositions of Earth, Moon, Mars, and Vesta (HEDs) are representative of the vast majority of rocky material in the solar system ($\Delta^{17}O \leq |0.3|$ ‰), the minimum initial gas $\Delta^{17}O$ is +8.6 ‰, as shown previously [7]; the minimum value for total gas $\Delta^{17}O$ of ~ 9 ‰ is a robust result.

Water $\Delta^{17}O$: The calculation can be extended to provide a constraint on the isotopic composition of H_2O. Thermodynamics and kinetics conspire to assure that the most stable oxygen-bearing species in the nebula was CO so that the nominal nebular H_2O/CO was 0.5. The oxygen mass-balance expression for the gas composed of CO and H_2O is then

$$\delta_{\mathrm{gas}} = f_{\mathrm{H2O}}\delta^{\mathrm{o}}_{\mathrm{H2O}} + (1 - f_{\mathrm{H2O}})\delta^{\mathrm{o}}_{\mathrm{CO}} \quad (2)$$

where f_{H2O} refers to the mixing ratio (oxygen fraction) for water and δ_{gas} is the oxygen isotopic composition of the gas in bulk (allowing for isotopic exchange between CO and H_2O at high T). The water $\Delta^{17}O$ value implied by equation (2) is +41 ‰ (for $\delta^{\mathrm{o}}_{\mathrm{CO}}$ = –24 ‰). This is a maximum based on the solar f_{H2O}.

Transport: H_2O/CO in the inner solar nebula should have risen above the baseline value of 0.5 by virtue of transport of H_2O ices inwards through the snowline. A simple equation that captures the essence of this process is

$$\Delta^{17}(t) \sim \Delta^{17}_{t=0}\exp(-kt) + \frac{J}{k}(1 - \exp(-kt)) \quad (3)$$

where k is the rate coefficient for net loss of ^{17}O and ^{18}O to condensed phases and J is the rate of advective addition of ^{17}O and ^{18}O. $\Delta^{17}O$ will reach steady state according to (4) on a time scale $4\tau = 4/k$. Estimates of k suggest τ on the order of years. To the extent that J is significant [1], we should expect that $\Delta^{17}O$ of H_2O was $\leq$ 41 ‰. We should expect further that changes in $\Delta^{17}O$ with time in the inner nebula resulted from variations in J.

Conclusion: High $\Delta^{17}O$ of nebular H_2O is a robust constraint on models for the oxygen isotopic evolution of the solar protoplanetary disk. Reaction networks are being constructed to test models for variable $\Delta^{17}O$ against the water $\Delta^{17}O$ and correlations with fO_2 implied by the meteorite data. Preservation of the slope-1 line in $\delta^{17}O$ vs. $\delta^{18}O$ space suggests that oxygen isotope exchange at high temperature was an important part of the nebular reaction network.

References: [1] Cuzzi J. N. and Zahnle K. J. (2004) *Astroph. J.*, 614, 490-496. [2] Lyons J. R. and Young E. D. (2005) *Nature*, 435, 317-320. [3] Young E. D. and Lyons J. R. (2003) *LPSC XXXIV*, 1923. [4] Marcus R. A. (2004) *J. Chem. Phys.*, 121, 8201-8211. [5] Krot A.N. *et al.* (2000) *Protostars and Planets IV*, 1019-1054. [6] Clayton R. N. (2002) *Nature*, 415, 860-861. [7] Clayton R. N. and Mayeda T. K. (1984) *Earth Planet. Sci. Lett.*, 67, 151-161.

OXYGEN ISOTOPIC CHARACTERISTICS OF REFRACTORY INCLUSIONS. H. Yurimoto[1], S. Itoh[1] and A. N. Krot[2], [1]Division of Earth & Planetary Sciences, Hokkaido University, Sapporo 060-0810, Japan (yuri@ep.sci.hokudai.ac.jp), [2]Hawai'i Institute of Geophysics & Planetology, University of Hawaii at Manoa, Honolulu, Hawaii 96822, USA.

Introduction: Refractory inclusions, which consist of Ca-Al-rich inclusions (CAIs) and amoeboid olivine aggregates (AOAs), have compositions corresponding to high temperature condensates from the solar composition gas [1]. Study of refractory inclusions started from CV3 chondrites, especially in Allende meteorite. Because the oldest age in the solar system has been determined in CAIs [2] and Al-Mg systematics suggest that this age also applied to other refractory inclusions [3,4,5], refractory inclusions should be key materials to study of origin of the solar system. In 1973, oxygen isotopic anomalies of ^{16}O-enrichment relative to the Earth have been discovered in refractory inclusions, indicating at least two oxygen isotopic reservoirs existed in the solar nebula [6]. Because oxygen is the third most abundant element in the solar system and the most abundant element of solid planets, study of the oxygen isotopic reservoirs is essential to understand material evolution in the solar system. Here we review oxygen isotopic characteristics among refractory inclusions and discuss possible situations of oxygen isotopic reservoirs in the solar nebula.

Classification of refractory inclusions: The CAIs are petrographically classified by mineral sizes and the texture. The CAIs whose minerals and textures are enough to be easily studied (>~50μm in size) with an optical microscope are named coarse-grained, and those that are too fine-grained to do so are named fine-grained [7]. Although the boundary between these two categories is not sharp, these nomenclatures are widely used. Coarse-grained inclusions are common in CV chondrites but are rare in other chondrite group. On the other hand, fine-grained CAIs are commonly distributed in all chondrite groups. Mineral sizes in AOAs are equivalent to those in fine-grained CAIs and the mineral assemblages continuously changes from fine-grained CAIs to AOAs. AOAs are also commonly distributed in all chondrite groups with higher abundance than fine-grained CAIs. Aqueous alteration in chondrite parent bodies easily affects fine-grained CAIs and AOAs, and disturbs their textures and mineral assemblages [8]. In this study our discussion focus to primary minerals prior to the aqueous alteration.

Oxygen isotopes of fine-grained CAIs and AOAs are uniformly enriched in ^{16}O (~5% excesses) for many chondrite groups [8,9,10,11,12]. The exception is only observed in CB, CR and CH chondrites. Oxygen isotopic compositions of fine-grained CAIs in CB chondrites are uniformly depleted in ^{16}O [13]. Those in CH and CR chondrites distribute from ^{16}O-rich to ^{16}O-poor, but individual inclusion has uniform value [14,15]. These characteristics indicate that most fine-grained CAIs and AOAs formed in ^{16}O-rich nebular environment but some was in ^{16}O-poor environment. Evidence of uniform oxygen isotopic composition for each inclusion suggests that they had simple thermal histories.

Coarse-grained CAIs were crystallized from Ca-Al-rich liquid droplets. Oxygen isotopes of coarse-grained CAIs heterogeneously distributes among minerals. The minerals at early- and late-crystallization stages are enriched in ^{16}O (~5% excesses), whereas those at intermediate crystallization stages are depleted in ^{16}O [16]. The heterogeneous oxygen isotopic characteristics indicate complex thermal history and different oxygen isotopic environments for the formation. Recent isotope point-analyses and isotope imaging for micro-area reveal that the ^{16}O-poor minerals formed at later heating stage in ^{16}O-poor nebular environment [16,17,18] and close genetic relation between CAI-rim and fine-grained inclusions [19].

References: [1] Grossman, L. and Larimar, J.W. (1974) *Rev. Geophys. Space Phys.* **12**, 71. [2] Amelin Y. et al. (2002) *Science* **297**, 1678. [3] Lee T. et al. (1976) *Geophys. Res. Lett.* **3**, 109. [4] Russell S. S., et al. (1998) *GCA* **62**, 689. [5] Itoh, S. et al. (2002) *Lunar Planet. Sci.* **XXXIII**, 1490. [6] Clayton R. N. et al. (1973) *Science* **182**, 485. [7] Grossman, L. (1980) *Ann. Rev. Earth Planet. Sci.* **8**, 559. [8] Itoh S. et al. (2004) *GCA* **68**, 183. [9] McKeegan, K.D. et al. (1998) *Science* **280**, 414-418. [10] Sakai, T., Yurimoto, H. (1999) *LPS* **30**, 1528. [11] Fagan, T. et al. (2001) *MAPS* **36,** 223. [12] Yurimoto et al. (2001) MAPS **36**, A230. [13] Krot et al. (2001) *MAPS* **36**, 1189. [14] Sahijpal et al. (1999) *MAPS* **34**, A101. [15] Aléon et al. (2002) *MAPS* **37**, 1729. [16] Clayton R. N. (1993) *Ann. Rev. Earth Planet. Sci.* **21**, 115. [16] Yurimoto H. et al. (1998) *Science* **282**, 1874. [17] Nagashima, K. et al. (2004) *In Chondrites and the Protoplanetary Disk*, 9072 [18] Krot, A.N. et al. *Nature* **434**, 998. [19] Krot, A.N. et al. (2002) *Science* **295**, 1051.

Notes

Notes

Notes